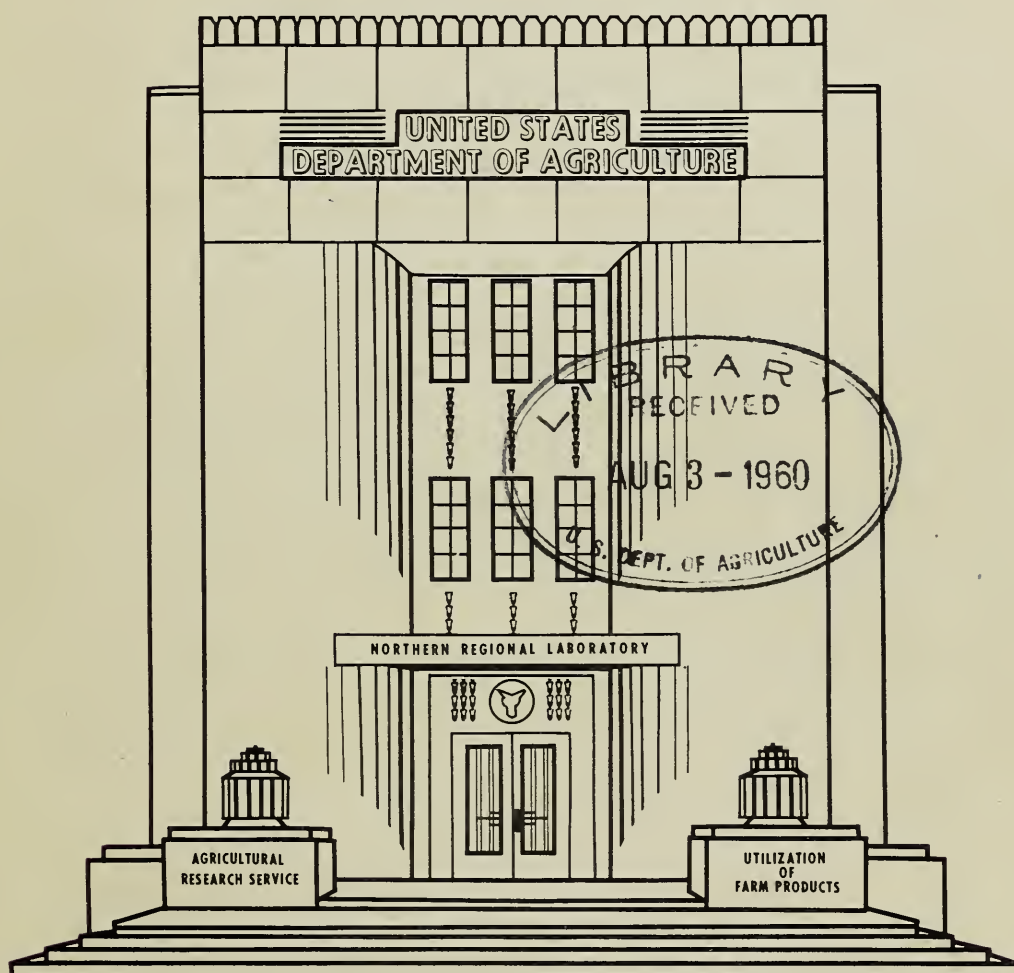


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March 1960

PROCESS TO RECOVER
MORPHINE FROM POPPY STRAW



Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE



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result of the process, material balances related to design of a commercial-size poppy-processing plant, and estimates of the capital investment for, and the operating costs of, such a plant.

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PROCESS TO RECOVER MORPHINE FROM POPPY STRAW

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I. INTRODUCTION

Morphine, one of our more important pain-relieving drugs, is one of the few that will relieve pain arising from internal organs. In sufficient amounts, it can allay pain almost completely. All medicinal morphine produced in the United States is obtained from imported opium, most of which comes from Turkey and India. In time of war or of world unrest, these imports may be reduced or cut off entirely. Cultivation of the opium poppy is forbidden in the United States except under license. The importation of opium and the recovery of morphine and other alkaloids from it has been restricted by law for many years.

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In time of war, pain-relieving drugs must be available for the treatment of battle casualties and if full-scale atomic warfare should ever occur, the demand for morphine for treatment of service personnel and civilians would be enormous. During the Korean conflict, the former Munitions Board of the Department of Defense believed that our imports of opium might be drastically reduced or cut off entirely and that it would then probably be necessary to recover morphine and other alkaloids from the dry capsules of mature domestically grown poppy plants. Because of the medical importance of morphine, the Munitions Board requested the U. S. Department of Agriculture: (1) To grow a supply of poppy seed in sufficient quantity to plant the required acreage needed in an emergency; (2) to develop a satisfactory recovery process; and (3) to make the preliminary design and cost calculations for a commercial processing plant for recovering the morphine in a form comparable to that present in opium.

The Northern Laboratory undertook development of the recovery process.

Opium is the dried juice or latex exuded from incisions made in the unripened capsules of the poppy plant, Papaver somniferum. Although the opium poppy has been grown for thousands of years, even today opium is obtained through much laborious and tedious manual work both in cultivation of the plant and in collection of the juice from fruits of the plant (3).^{4/} Some 22 alkaloids are found in opium, but only four--

^{4/} Italic numbers in parenthesis refer to Literature Cited p. 94.

morphine, codeine, thebaine, and papaverine--are of commercial importance. The amount of morphine varies over wide limits, but in a good grade of opium the content averages 10 to 12 per cent. The three minor alkaloids are present in opium in considerably smaller and in varying amounts depending on the country of origin.

Interest in cheaper methods for producing morphine led to the development of more modern processes that were put into commercial operation on a very limited scale in Germany and Hungary in the 1930's. E. Merck A.G., Darmstadt, Germany, erected a pilot plant in 1936-37 that was operated as a production unit during World War II by a mandate from the German Government. In the Merck process, morphine is extracted from poppy meal with chloroform and the extract is passed through an aqueous solution of phosphoric acid. The aqueous solution is made slightly acid to litmus and is concentrated about fourfold by vacuum evaporation, then the morphine is precipitated by addition of ammonia (7).

Frey and Wüest developed a process in Switzerland in the early 1930's for the countercurrent extraction of opium alkaloids from ground straw with lime water. After the water extract is made less alkaline, the alkaloid bases are extracted by an immiscible organic solvent, and either the solvent is removed by distillation or the alkaloids are transferred to a dilute acid solution (8).

János Kábay, a Hungarian, patented a process a few years earlier wherein the extraction is made with dilute mineral acid, particularly sulfurous, and the extract liquor concentrated by vacuum evaporation. After removal of proteins and saccharides, the morphine is precipitated but the yield is low (12).

Although a number of patents and other information in the literature (1, 2, 10, 16, 28) relating to the recovery of opium alkaloids from poppy straw and capsules were studied, available information on the degree of morphine recovery attained by any of the processes was meager and usually indefinite because of omission of some of the essential data. It was apparent that each of the processes had certain shortcomings.

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Consequently, research on the recovery problem was initiated at the Northern Laboratory with the following specific objectives: (1) Select suitable facilities for storage of the poppy straw and develop a satisfactory method of preparing it for the extraction step, (2) develop a continuous method for extraction of morphine from the meal, (3) develop a suitable method for recovering morphine from the extract liquor, (4) evaluate the product, (5) make the preliminary design for a commercial-size processing plant to produce crude morphine liquor from which 60,000 pounds of medicinal-grade morphine can be obtained annually, and (6) make an estimate of the capital investment and operating costs.

II. SUMMARY

Based on pilot-plant studies, a commercial process has been developed and preliminary design calculations made for a plant to produce sufficient crude morphine liquor from poppy straw to yield the desired 60,000 pounds per year of morphine. By this process crude poppy straw harvested from P. somniferum is processed through a preliminary milling operation during the 3-week harvest season to remove the seed and many stems prior to storage of the capsular material. This stored straw is converted into a meal by further milling operations, 69 pounds of meal being obtained from 100 pounds of the crude straw.

After treatment with ammonia to liberate the morphine and other alkaloids from their salts within the plant material, 95 percent of the morphine is extracted from the meal by a water-saturated solution of isobutyl alcohol (IBA) in a continuous countercurrent extractor.

Morphine in the IBA extract is adsorbed on a cation exchanger, the exchanger is washed with 91 volume percent isopropyl alcohol (IPA) to remove interfering tars, and the alkaloids eluted with a 4-percent sodium hydroxide solution. The eluate is concentrated by vacuum evaporation to produce the crude morphine liquor, which contains about 86 percent of the morphine from the poppy meal. The liquor from this commercial process is composed of about 20 percent total solids. It should contain about 1.6 percent morphine and 0.25 percent codeine by a morphine refiner's assay and should be a suitable raw material for the production of medicinal-grade morphine and codeine. A 90-percent recovery at the morphine refinery is assumed.

The overall yield, as calculated by the method used by the United Nations Permanent Central Opium Board, is 30 tons of anhydrous morphine from 10,910 tons of poppy straw, or 0.27 percent.

The estimated capital investment for this poppy-processing plant is \$3,766,000. Almost \$11 million will be needed annually to purchase the required poppy straw. The estimated production cost for the crude morphine liquor, excluding administrative and related costs, is \$10.25 per ounce of anhydrous morphine, which includes a charge of \$10.24 for crude poppy straw, \$1.01 for other materials, labor, utilities, etc., and a credit of \$1.00 for byproduct codeine valued at \$6.00 per ounce. An additional saving of up to about 15 cents per ounce of morphine may be obtainable by using several cation exchangers in series.

The process described has been designated the ion-exchange recovery method. A second method employing distillation to vaporize the IBA was also studied, but a comparative cost analysis indicated that the ion-exchange method had the lower production cost.

III. PILOT-PLANT INVESTIGATIONS

A. Analytical Methods

The Matchett and Levine method for determining morphine (17, 19) was used for most samples because many of the various poppy plant fractions and process streams contained no more than 5 milligrams of morphine in portions of convenient size for analysis. The U. S. Pharmacopeia method requires about 600 milligrams of morphine and the Association of Official Agricultural Chemists (AOAC) method requires about 160 milligrams (23).

A ferricyanide method was occasionally used for a rapid and approximate estimation of morphine content during experimental operations. This method was developed at our laboratory by C. L. Mehlretter and is a modification of Hanes' ferricyanide micromethod for reducing sugars (4). The method was based on the reduction by morphine of potassium ferricyanide to ferrocyanide in alkaline solution and determination of the excess ferricyanide by thiosulfate titration of iodine liberated upon addition of potassium iodide solution. To standardize the method, titrations were made with solutions containing known amounts of morphine and tables were prepared both for IBA and aqueous solutions wherein morphine content expressed in milligrams was listed against the corresponding titer of 0.01 N sodium thiosulfate. Although the ferricyanide method was known to include reducing materials other than morphine, it was helpful in the pilot-plant operations.

The Matchett and Levine method is not specific for morphine and the resultant values are high (30). For comparison, arrangements were made with a commercial morphine refiner, the Mallinckrodt Chemical Works, to have analyses made of duplicate samples. This refiner used a modified U. S. Pharmacopeia method to analyze the IBA extract and the crude morphine liquors; a special method was used for the poppy meal (11). As noted later, Mallinckrodt's values were considerably lower. In spite of the difference, excellent agreement was obtained in the percentage of morphine extracted from the poppy meal calculated by either method.

All experimental data reported under "Pilot-Plant Investigations," in Tables 1-20, 32-45, and Figures 2-11 are based on the Matchett and Levine analyses unless stated otherwise. For design of the commercial-size plant, a correction factor was employed to compensate for the difference between the two methods (see Table 33). Production costs and related estimates are based on the production of a specified quantity of morphine based on Mallinckrodt's assay.

All analytical values for morphine, codeine, and thebaine content are reported as the anhydrous alkaloid.

The water content of IBA solutions was determined by a simple distillation with the water being distilled as an IBA-water azeotrope. From a correlation with the distillate's specific gravity, the water content of the sample was calculated.

Other analyses were made by conventional procedures used for agricultural products.

B. Preparation of Poppy Meal

P. somniferum, variety No. 40, was grown under irrigation by the Field Crops Research Branch of the U.S. Department of Agriculture. At maturity, the crop was harvested by use of a conventional small-grain combine with minor modifications. The combine produced three fractions: (1) Poppy seed; (2) a mixture of capsules, stems, and some seed, hereinafter referred to as crude straw; and (3) stems and leaves which were returned to the harvest field (25).

The highest concentration of morphine is found in the capsule of the poppy plant. Morphine is also found in low concentration in the stems, but there is none whatsoever in the seed (10, 29). A visual examination of the crude straw (Figure 1) delivered by the combine indicated that much less material need be processed if a satisfactory method could be found for separating stems from the capsules. Since the straw must be stored to protect it from rain, removal of stems would result in considerable savings in the investment for storage facilities. Further savings could be expected in the cost of process equipment for handling the solids.

Methods of separating stems and seed from the capsular material were studied. The seeds should be removed because their oil causes difficulties in purifying the morphine. Various machines were tested for properly breaking the capsules without cutting the stems so severely that the two could not be separated by screening or in some other simple way. Most machines were too severe either in their cutting action or in crushing and tearing the stems.

Promising results were obtained with a corrugated roller mill built for grinding grain. The capsular material was broken into smaller pieces while the stems were flattened but not cut too severely. After being freed of stems, the broken capsules could not be rolled and flaked satisfactorily as is customarily done with oilseeds prior to solvent extraction; consequently, they were ground into a meal passing a 20-mesh sieve to facilitate extraction.

Several experiments were made under the supervision of Mr. George Jennrich at the Allis-Chalmers milling laboratory in Milwaukee. Preliminary trials showed that rolls with LePage corrugations would be most satisfactory for the first break. These rolls effectively freed the capsules from the stems and broke the nodes without damaging the stems excessively. In further experiments it was learned that the best separation was made by use of a four-break milling system whereby the straw is gradually reduced in size with stems being removed by a sifting operation after each grinding step. Satisfactory yields, separations, and mill loads were obtained by use of the milling conditions given in Table 1 and the flow diagram shown in Figure 2. The proportion of meal obtained in each of the four steps is given in Table 2.

Several lots of poppy meal were prepared at the Northern Laboratory by the four-break milling procedure developed in cooperation with the Allis-Chalmers Manufacturing Company. The last of these lots, MS-7, was prepared from 4,275 pounds of crude straw with results comparable to those expected from commercial operations. For the first break in this milling procedure an Allis-Chalmers experimental roller mill equipped with LePage corrugated rolls measuring 6 by 6 inches and having 5 corrugations per inch, was employed. A 3-pair high Robinson roller mill with 9 by 18-inch conventional corrugated rolls was used for the 3 succeeding breaks. These rolls operated sharp-to-sharp but the cutting edges were dull. Normally, only one pair of rolls with proper corrugations and speed differentials need be used for each break but because of the limitations of our equipment, it was necessary to use the top pair of rolls in this mill for the second break, the upper two pairs for the third break, and all three pairs for the fourth break. The top pair had 8 spiral-cut corrugations per inch; the middle pair, 12 per inch, and the bottom, 20 per inch. The milled streams were separated into 3 fractions in a Robinson grain cleaner, size 2U, which was equipped with round-hole perforated screens and operated without aspiration. A rotary knife cutter, Abbe' Mill size No. 000, was used to regrind some stock from the seed-bearing fraction and from the fourth break. All of this equipment was operated intermittently, but the flow of materials was similar to that used in continuous processing operations. The seed-bearing fraction was cleaned in a Hero fanning mill and an Eureka bean cleaner.

The resultant poppy meal constituted 69.0 percent of the crude straw. A material balance covering each step in the milling operation, including the separations made and the yields obtained, is given in Table 3. When loosely packed, the meal had a bulk density of about 13 pounds per cubic foot at a moisture content of 9 percent. The sieve analysis of the meal is shown in Table 4. Bulk densities of the crude poppy straw and of the various straw and meal fractions are listed in Table 5.

Morphine contents of the discarded stems and of the poppy meal from lot MS-7 are shown in Table 6. The morphine lost in all discarded stems totalled only 5.7 percent of that present in the crude straw. Weight of meal to be extracted was decreased about 22 percent by removal of these stems and another 7 percent by removal of seed while the morphine concentration of the meal was increased from about 0.5 to 0.7 percent.

Storage tests of the poppy meal in both open and sealed containers kept at room temperature and in an unheated barn showed no loss of morphine in 2 years. As long as the straw or meal is kept dry, it can be stored for use throughout the year without loss of morphine.

C. Extraction Operations

Countercurrent Solvent Extraction

Although concentration of morphine in the poppy meal is relatively low, Mehlretter and Weakley learned in their laboratory studies that a high percentage of the morphine could be extracted in 1/2 hour, which is well within a practical range for continuous extraction (19, 20, 21).

Equipment and procedure.---Poppy meal previously wetted with extract liquor was fed by a gravimetric feeder through a screw conveyor into a continuous countercurrent extractor with 20 extraction stages. Poppy meal was introduced at stage 1 and two solvent streams were used, one entering at stage 20 and the other between stages 16 and 17. The extractor was of the Kennedy type (13, 14) with the body inclined $1^{\circ}34'$ from the horizontal; the solids inlet was at the lower end. Solids were moved through the extraction stages (a series of round-bottomed troughs) by impellers 12 inches in diameter and 9-1/2 inches wide, made with 3 straight blades which were slotted at the outer end and offset from the axis of rotation. The extracted solids were drained for approximately 7 minutes on an inclined flight conveyor. Extract liquor was filtered through a cloth bag made from cotton duck, style No. 8, for removal of "fines" (suspended solid particles). The bag had about 2 square feet of filter area and was changed after 10-20 hours of operation.

The extraction equipment was operated on a continuous basis for periods of 20 to 24 hours. During this time a 12-hour interval was taken as a test period which began 6 to 8 hours after the extractor was started; this was ample time to reach steady-state conditions. Quantitative data and samples were obtained and extract liquor was collected in a separate tank during the test.

Before the poppy meal was fed into the extractor, 6-pound batches were prewetted with 10-15 pounds of fresh extract liquor to which 150 milliliters of aqueous ammonia (25.3 percent NH_3) had been added. The mixture was allowed to soak for 1 to 1-1/2 hours to reduce the quantity of fines carried out in the extract liquor while the ammonia liberated alkaloids from their naturally occurring salts within the plant material and thus facilitated their extraction.

A process giving adequate extraction was used but no attempt was made to study the influence of variables such as extraction temperature, quantity of ammonia used to treat the meal, and fineness of grind for the poppy meal. A diagrammatic flowsheet for the extraction and pressing operations used is shown in Figure 3. Typical flow rates, process conditions, analytical values, and material balances established after a number of exploratory runs are given in Tables 7-9.

Extraction efficiency.--For the last 15 pilot-plant tests, morphine present in the extract liquor varied from 86 to 98 percent of the quantity present in the poppy meal. In the first 11 tests of this group, 233 pounds of wetting liquor were used per 100 pounds of poppy meal and the extraction averaged 89.7 percent. In the 12th test the quantity of wetting liquor was reduced to 200 pounds and in the last 3 to 167 pounds. In these last 4 tests, 95.4 to 98.0 percent of the morphine was extracted (averaging 96.9 percent), and a simultaneous reduction in the amount of "fines" removed from the extract liquor was also noted. The reason for the increased extraction was not ascertained, but it may result from the prewetting treatment.

Duplicate samples of extract liquor and poppy meal from one of the first tests in this series were analyzed for their morphine concentration by the Mallinckrodt Chemical Works (11). Their values, given in Table 10, were just under 70 percent of those obtained by the Matchett and Levine method. However, the agreement in percentage of morphine extracted was satisfactory. Based on our analyses, 85.6 percent of the morphine was extracted, and by Mallinckrodt's analyses, 88.6 percent.

These samples were also analyzed for their codeine and thebaine contents by the Mallinckrodt Chemical Works (11), and the reported values are given in Table 11. A total of 84.0 percent of the codeine and 82.7 percent of the thebaine was extracted. Thus, the extraction process removes each of these alkaloids to essentially the same degree as morphine.

A typical extraction profile is shown in Table 12. To obtain this profile, each of the liquid samples was filtered through filter paper to remove suspended solids. To minimize deposition on the meal solids of any morphine present in the entrained IBA solution, each sample of solids was placed in a towel, wrung free of as much entrained liquor as possible, washed once on a Büchner funnel, and dried at 140° F. for 2 hours in a forced-draft oven. A pentane-hexane mixture was used for the washing step since morphine is practically insoluble in this solvent. The necessity for this washing step is indicated by the results of a test made on a sample of fines removed from the extract liquor. One-half of the sample was dried and found to contain 0.58 percent morphine. The other half, when washed with pentane-hexane prior to being dried, contained 0.32 percent morphine.

Although the morphine contents given in Table 12 for solids removed from various stages of the extractor are not absolute values, they are indicative of the concentration gradient for morphine throughout the extractor and of the rate at which morphine was extracted. About 20 stages were required under the conditions used to extract most of the morphine. In this particular test, 90.3 percent of the morphine in the poppy meal was recovered in the extract liquor, while a calculation based on reduction in morphine content of the solids indicates better than 94 percent extraction. The inaccuracy of the analytical method at low morphine levels can easily account for this difference.

Solvent ratio and other extraction factors.--An overall solvent-to-meal ratio of 6.7 to 1 was used in all extraction tests reported in this publication. In these tests press liquor recovered from the extracted meal was returned to the Kennedy extractor between stages 16 and 17 as a secondary solvent. The primary solvent-to-meal ratio was thus reduced to 4.5 to 1 without any loss in extraction efficiency as compared to earlier runs where a 6.7 to 1 primary solvent ratio was used and no press liquor was returned.

The primary solvent, i.e., solvent A, was a water-saturated solution of IBA recovered from various sources. It contained some morphine, averaging 0.002 percent. Solvent B contained about 0.009 percent morphine.

Poppy meal was retained within the extractor for $3\frac{1}{4}$ hour which is believed about right for the conditions used although the optimum holding time was not determined.

Fines in the extract liquor averaged 2.23 pounds (air-dry solids) per 100 pounds of poppy meal fed to the extractor and varied from 1.73 to 3.16 pounds. The average value decreased to 1.87 pounds in the last four tests in which less wetting liquor was used. Although more than 50 percent of the fines passed a 100-mesh sieve and 30 percent went through a 325-mesh screen, as shown in Table 13, no difficulty was encountered in the filtration step.

This quantity of "fines" was high in comparison with that normally encountered in the extraction of soybeans. However, the method employed for separating stems from the capsular material, and for grinding the capsules, leaves some pithy material in the meal. This pithy material does not become saturated with solvent even after a prolonged soaking period and its low density makes this material float readily. The presence of pithy material probably increased the porosity of the filter cake and thus improved the filtration rate.

From the data given in Table 8, it is noted that while solvents A and B contained 15-16 percent water, the extract liquor contained only 6-1/2 percent. It is apparent that the poppy meal adsorbed water during the extraction step in preference to IBA.

Other Types of Extractors

Because of the quantity of fines obtained and the fineness of the meal to be extracted, consideration was given to other types of extraction equipment. Laboratory tests were made to determine the rate at which solvent would percolate through a 24-inch bed of the poppy meal in a 2-inch I.D. glass column. Percolation rates of 60 to 100 pounds per hour per square foot were obtained, but since the usual percolation rate for commercial operations is in the range of 1,600-3,000 pounds per hour per square foot (6), it appears that the meal, as ground for these tests, is not suitable for percolation-type extractors.

A new sample of meal was separated into three fractions as follows:

<u>Fraction</u>	<u>Percent</u>
Passing 6-mesh, retained on 12-mesh sieve-----	29
Passing 12-mesh, retained on 30-mesh sieve-----	49
Passing 30-mesh sieve-----	<u>22</u>
Total-----	100

With solids from the intermediate fraction, a percolation rate of 2,365 pounds per hour per square foot was obtained, and this rate was increased to over 3,000 pounds when the two coarser fractions were blended together. However, upon blending all three fractions, the percolation rate fell off drastically to 200-275 pounds per hour per square foot. For operation of percolation-type extractors, the poppy meal should not be ground to a degree where much of it passes a 30-mesh screen, and to obtain adequate extraction of the morphine it may then be necessary to use a prolonged extraction time.

In another test, poppy meal was wetted with IBA extract and after 1/2 hour the mixture, with an excess of extract liquor, was placed in a wide-mouth centrifuge bottle and centrifuged for 5 minutes under a force about 1,000 times gravity. Most of the solids were compacted at the bottom of the bottle, but a small layer of light, pithy solids separated to the top. Each layer was carefully removed, air-dried, and weighed. The pithy solids constituted approximately 3 percent by weight of all the solids. Because of the formation of two distinct solid phases, an extraction system employing centrifuges for separation of the meal and liquor would require additional centrifuges.

For the filtration-extraction process a mass velocity of 2,000 pounds per hour per square foot of filtration area in bench-scale tests is said to be the minimum practical flow rate for liquor through a 2-inch cake under a vacuum of 4 inches of mercury (9). This mass velocity is predicated on a solvent-to-meats ratio of 1.2 to 1 and on a reasonable capacity for equipment used to extract cottonseed. When higher solvent ratios are required, a higher mass velocity should be attained if solids-handling capacity of the equipment is to remain unchanged. Mass velocity tests on the poppy meal from lot MS-7 were made with extract liquor and a Büchner funnel equipped with a 24 by 110 Dutch-weave screen. With a cake 2 inches thick, the following results were obtained:

<u>Vacuum</u>	<u>Temperature</u>	<u>Mass Velocity</u>
<u>Inches Hg.</u>	<u>°F.</u>	<u>Pounds per hour per square foot</u>
1	Room	625
1-1/2	Do.	750
2	Do.	850
4	Do.	1,100
4	140	2,100

For these tests, 6 pounds of the meal was mixed with 10 pounds of wetting liquor $1\frac{1}{2}$ hour before the tests were made. When the mixture of meal and liquor was set aside for 60 hours before the filtration rates were determined, mass velocities of 1,300-2,000 pounds per hour per square foot were obtained at room temperature and a 2-inch vacuum. These results indicate that the filtration-extraction process can be used; presumably the required solvent ratio would be lower than that used in a Kennedy extractor.

Pressing the Extracted Meal

The extracted meal was pressed in a Davenport continuous dewatering press, size 3A, equipped with revolving disks 42 inches in diameter, and operated at the lowest speed, 0.51 r.p.m. Each disk was fitted with strainer plates covered with brass screens having three $\frac{1}{4}$ -inch perforations.

Wet marc containing about 80 percent moisture and volatile matter was reduced to about 60 percent volatile content when fed to the press at a rate of approximately 2,800 pounds per hour. This is equivalent to a reduction from 4.0 to 1.5 pounds of volatile material per pound of dry solids. Several tests were at feed rates of about 6,100 pounds per hour but considerably less press liquor was obtained, that is, 179 pounds per 100 pounds of poppy meal fed to the extractor as compared with 229 pounds with the lower feed rate. In all tests, difficulty in feeding the press was encountered because of material bridging in the feed hopper.

An experiment with a laboratory-sized hydraulic press was made to learn what further reduction in volatile content could be produced by the application of pressure. The curve in Figure 4 indicates that a considerable reduction in the volatile content is obtained as pressure is first applied, and that the Davenport press develops a pressure of approximately 100 p.s.i. If the pressure in this or some other press were increased to 300 p.s.i. and the necessary drainage time obtained, the volatile content of the meal could be further reduced to 52 percent. This would decrease the load on the desolventizing equipment by one-fourth.

D. Morphine Recovery from Extract Liquor

Two methods were investigated for the recovery of morphine and other opium alkaloids from the isobutanol extract. In one method the recovery was by ion exchange while in the other, distillation was used to separate the solvent. In both cases aqueous solutions of the alkaloids and other solids were produced. These solutions were concentrated by evaporation under vacuum to give crude morphine liquors suitable for shipment to a morphine refining plant.

Recovery by Ion Exchange

Mehltretter and Weakley (19) ascertained that a cation exchanger of low cross-linkage can be used to recover morphine quantitatively from the IBA extract and that the anion effluent can be re-used for extraction of alkaloids from the poppy meal. Duolite C-10, a synthetic sulfonated resin which can adsorb large organic molecules, was used as the cation exchanger in the pilot-plant operations.

Equipment.--Two ion-exchange columns, one cation and one anion, were employed in the recovery study. The cation-exchange column, constructed of 12-inch O.D.-type 304 stainless-steel tubing 10 feet long, was partially filled with Duolite C-10 exchanger whose backwashed, settled, and drained volume in the acid-regenerated state was 4.0 cubic feet (bed depth = 66.5 inches). The resin was supported on an 80-mesh, stainless-steel screen mounted 8 inches above the bottom of the column and was aerated during certain process steps by compressed air fed through a 1/4-inch pipe coil located about 3 inches below the support screen. Deionized water for washing the upper walls entered through a similar pipe coil placed near the top of the column. A disk at the end of the feed pipe ending about 6 inches above the resin bed minimized disturbance of the bed by the incoming feed. Effluent passed out of the bottom of the column through an overflow leg which elevated the liquor approximately 6 inches above the bed level. Two vertical rows of holes drilled 180° apart in the upper and lower sections of the column and sealed with a fairly transparent Tygon sheet were used to observe the interior of the column.

Prior to beginning the test runs, the fresh cation-exchange resin was conditioned through three complete cycles according to the recommended procedure of the manufacturer by exhausting it completely with 4-percent sodium hydroxide solution and regenerating it with 5 percent sulfuric acid.

The anion column consisted of a glass pipe 6 inches I.D. by 10 feet long. Other design features for this column were similar to those used in the cation column. The backwashed, settled, and drained volume of the Duolite A-7 bed after regeneration with sodium hydroxide was 0.57 cubic feet; the depth of the bed was 35 inches. The anion resin was also conditioned before it was used in the pilot-plant tests.

Experimental procedure.--The diagrammatic flowsheet, Figure 5, illustrates operation of the recovery process by ion exchange. The IBA extract, pH 7.7 to 8.4, from the Kennedy extractor was first filtered through a horizontal plate filter. The volume of liquor fed to the cation column was about 100 gallons and in a majority of the tests contained 21 to 25 ounces of morphine (Table 14).

Feed liquor was pumped through a rotameter into the top of the cation column at a rate of 1.57 gallon per minute per square foot. Water covering the resin was displaced and diverted to the sewer. When IBA effluent reached the outlet, it was collected temporarily in a 5-gallon container and then pumped into the top of the anion column where the water was displaced similarly. Near the end of the adsorption period, an increase in resistance of the cation resin bed was observed. The desired flow rate was maintained by use of nitrogen gas at a pressure of $1/2$ - to $1-1/2$ -pounds per square inch gage in the head space above the resin. At the end of the operation, the pressure was increased slightly to push liquor out of the cation column. Liquor remaining in the anion column was drained by gravity. About $1-1/2$ hours were required to process all of the IBA extract through both columns when the cation and anion columns were operated in series.

After a 20-minute drainage period, the cation resin was washed by pumping in 88 pounds of an alcohol (see Table 15 for specific type) by upflow; this quantity was sufficient to cover the bed. The mixture was aerated vigorously for a period of 10 minutes by compressed air, and the column was drained.

Elution of the resin bed was conducted by pumping 21.8 gallons of 4-percent NaOH solution at 6.93 gallons per minute per square foot into the column by upflow and again aerating vigorously for 10 minutes. The liquid level was then lowered to approximately 6 inches above the resin bed and the alkali solution and resin adhering to the upper walls were rinsed off by means of the water spray. The alkali solution was displaced by downflow at a rate of 1.57 gallons per minute per square foot with a total of about 75 gallons of rinse water and the column was drained. Displaced eluate leaving the bottom of the column was, for convenience, usually collected in three fractions. Concentrated H_2SO_4 solution was added immediately to each fraction to adjust its pH to approximately 6.5-7.0.

Immediately following elution, the cation exchanger was regenerated by pumping 21.8 gallons of 5-percent sulfuric acid solution into the column by upflow at 6.93 gallons per minute per square foot, followed by aeration and rinsing as for the elution step. Rinsing was continued until the pH of the effluent was approximately 3.5, thus completing regeneration of the cation column.

The anion column, which already had been drained for almost 30 minutes following completion of the exhaustion step, was regenerated by a similar procedure using 15.3 gallons of 1-percent NaOH solution. Rinsing was carried out to an effluent pH of approximately 9.0. In several tests it was necessary to backwash the resin for a few minutes to remove some scumlike solids that appeared after aeration in the regeneration step, but the need for this eventually disappeared with continued use of the alcohol-wash procedure, as will be explained on page 41.

Deionized water was used for all aqueous solutions passed through the anion column and for the solutions used in regeneration of the cation column.

Adsorption of morphine. --Data are given in Table 14 on the reduction of morphine concentration in the IBA extract as it passed through the cation and anion columns. In most runs the morphine content was reduced to less than 0.005 percent in the effluent. The slight decrease in concentration observed as the stream passed through the anion column is attributed to adsorption rather than to ion exchange. In each case the IBA effluent from the anion column was sufficiently low in morphine to permit its re-use for extraction of alkaloids from the poppy meal.

Data on the quantity of morphine adsorbed from the IBA extract in each run by the cation exchanger are also tabulated in Table 14. The average adsorption was 98.8 percent for the last seven runs where suitable conditions had been established. In one of the early tests, No. 17, the influent contained more than the usual amount of morphine and this presumably reduced the degree of adsorption while the low adsorption for tests 19 and 20 is attributed to an accumulation on the exchanger of tars and similar interfering materials. No specific reason can be given for restoration of adsorptive capacity in test 21 prior to use of the alcohol-wash step unless improvement was brought about in test 20 where a much larger quantity of rinse water was used in the elution step.

In Figure 6 the morphine adsorbed per cubic foot of cation resin in these runs is plotted against the total influent. This substantially straight-line relationship shows that the total capacity for morphine was not reached in any run.

Breakthrough or leakage of morphine into the cation effluent during the adsorption step was measured during test 26. Analyses of five spot samples of the effluent taken at intervals are plotted in Figure 7. The concentration of alkaloid remained low until over 50 gallons had been collected. At this point the concentration began to rise rapidly and continued to do so for the remainder of the test. Although the last sample had a concentration of 0.02 percent, that for the cumulative effluent (96 gallons) was only 0.004 percent. It is evident that upwards to 99.9 percent of the morphine can be adsorbed by using two or more columns in series and by diverting the stream to a fresh column when morphine is detected in the effluent. In this manner the resin in each column can be very nearly saturated prior to elution and the exchanger will adsorb more morphine per unit volume than was done in any of these tests.

The curve in Figure 7 is indicative of the typical breakthrough curve which is sigmoid in shape. When plotted on arithmetic probability paper, such a curve is transformed into a straight line. Thus, the data in Figure 7 have been replotted in Figure 8 and can be extrapolated. According to Samuelson (26) an appropriate measure of the total capacity of the exchanger may be based upon the volume throughput when concentration in effluent divided by concentration in influent equals 0.5 percent. In Figure 8, about $4\frac{3}{4}$ volumes of liquor per volume of resin corresponds to $C/C_0 = 50$ percent. With the IBA extract containing 0.203 percent morphine, the total capacity of the Duolite C-10 exchanger was calculated to be approximately 7.94 ounces morphine per cubic foot of resin as compared with the 5.65 ounces per cubic foot attained with one column in the last seven pilot-plant tests.

As cations other than alkaloids are adsorbed by the cation exchanger, both organic and inorganic acids accumulate in the effluent and their concentration should vary as the adsorption proceeds and should change the pH and the conductance accordingly. Thus, measurement of one of these might serve as a convenient method to ascertain when the cation exchanger no longer adsorbs morphine to an adequate degree.

It is desirable to load the cation exchanger with as much morphine as possible during each adsorption step. The monetary value of morphine and codeine makes a high degree of recovery mandatory, but the very nature of ion exchange in columnar operation is such that the percentage of adsorption decreases progressively during the exhaustion step. Close and constant control will be necessary to maintain a reasonable relationship between adsorptive capacity and recovery. The data from several tests indicate that pH readings of initial portions of the effluent either remain constant or decline and then rise for succeeding portions. If the adsorption step is carried sufficiently far, the effluent pH will approach that of the influent. The first rise in pH correlates approximately with the appearance of morphine in the effluent and probably can be used as a control procedure.

Alcohol washes.--The decline in percentage of morphine adsorbed in tests 19 and 20 was attributed to deposition of tars and other alcohol-soluble materials on the resin, thus reducing the surface area for adsorption and elution. Analyses made in later tests showed a decrease in total solids from 2.0 percent in the cation influent to 0.95 percent in the anion effluent. These data and an analysis of the cation effluent from one test suggest that practically all of the reduction takes place within the cation column. Almost three-fourths of the solids in the cation influent were soluble in petroleum ether and practically all in the anion effluent. As a remedial treatment, the use of an alcohol wash between the adsorption and elution steps to dissolve and remove these tars was found helpful. Of the various alcohols used, IPA, 91 volume percent, was considered most practical (Table 15). Considerable foaming was encountered during aeration in the elution step when methyl alcohol was used, and the foaming was reduced by addition of octyl alcohol. No antifoam agent was needed with the 91 volume percent IPA.

Solids content of the spent IPA wash varied from 1.2 to 1.4 percent with almost one-half of these solids being soluble in petroleum ether. As a comparison between IBA (0.4 percent maximum water content) and 91 volume percent IPA in their ability to dissolve these solids, a test was made using equal volumes of these two alcohols to redissolve solids obtained from the spent IPA wash. While the solids redissolved completely in the IPA, they did not in the IBA and, in the latter case, the rate of solution was slower. It was concluded that IPA was the better solvent for removal of tars from the cation exchanger.

The quantity of morphine that supposedly was dissolved in the alcohol washes is given in Table 15 and accounts for roughly 3 to 10 percent of the morphine adsorbed by the cation exchanger. However, these values are subject to considerable question since the samples were difficult to analyze because of the tars present. A procedure discussed later under the distillation recovery method possibly could be used to recover much of the morphine present in tars that remain after evaporation of the alcohol, or presumably the tars could be dissolved in hexane and the alkaloids extracted with water-saturated IBA.

Elution of morphine.--In the first several tests only about 87 percent of the adsorbed morphine was eluted. In test 19, a larger volume of rinse water was found to increase the degree of elution substantially to 97.6 percent. The eluate volume in this case was 90 gallons while in preceding tests it had been 60 to 70 gallons. Accordingly, it was estimated that about 95 gallons of eluate were required for essentially quantitative elution and this quantity or more was collected in a majority of the remaining tests. Even so, considerable variation was encountered in the percentage of morphine eluted. The elution was as low as 83 percent in one test, as high as 112 in another, and in 3 of the last 4 tests it was over 100, suggesting a possible buildup of morphine on the cation exchanger in the preceding tests. The average elution for all 12 tests was 96 percent.

In test 21, six consecutive portions of the eluate were collected and the morphine content of each is given in Table 16. Most of the morphine was removed in the first fraction. A very rough calculation based on steam and water costs for the evaporation step and an assumed value of \$6 per ounce for the morphine indicates that the value of the morphine was much more than costs of the steam and water until about 140 gallons of eluate were collected.

The first eluate fraction obtained from the cation exchanger was dark in color. As the rinsing continued, the eluate became progressively lighter in color and near the final stages reached a light-amber color. Upon standing, the first batch of the eluate usually became covered with a thin tarlike floating layer and upon neutralization with sulfuric acid, a flocculent precipitate was formed. The second fraction formed a brown scum upon acidification and none generally appeared in the third. The tarlike material in the first and second fractions was small in quantity, but it did gather and cling to the walls of the tank. After the alcohol-wash procedure was adopted, the quantity of tars and precipitated solids appeared, by visual observation, to decrease.

The eluates contained significant quantities of alcohol.

Anion column and general information.---Operation of the anion column was satisfactory. Reasonably good de-acidification of the IBA influent was accomplished. For the last 10 tests, where a fairly uniform quantity of extract liquor was processed, the pH of the anion effluent tested 6.0 to 6.7. This effluent was also essentially saturated with water (specific gravity, $30^{\circ}/15^{\circ} \text{ C.} = 0.833$).

During regeneration of the anion exchanger, particles of a green, flocculent, scumlike solid were observed on top of the resin bed immediately following the aeration. The largest quantity was noted in tests 19, 20, and 21, and the amount became progressively smaller in succeeding tests. These solids were removed by backwashing the column at a rate of 1.7 gallons per minute per square foot. For tests 26 and 27, the solids formed were so small in quantity that backwashing was not required. When an alcohol rinse of the cation exchanger was used, little or no precipitate was obtained in the anion column.

A check was made on the loss of morphine in the spent regenerant solutions from both the anion and cation beds. The quantity involved was negligible.

Data were obtained on the change in volume of both the cation and anion exchangers during a complete cycle. The volume of resin in the backwashed, settled, and drained state after regeneration was used as the datum point. For the cation resin, the volume decreased 13 percent in the exhaustion step and increased to 12 percent above the datum point after aeration in the elution step. The volume of the anion exchanger decreased 7 percent during the exhaustion step and increased 7 percent in regeneration.

Concentration of cation eluates by evaporation.--The unfiltered eluates were concentrated batchwise under 28-29 inches vacuum in a 50-gallon jacketed kettle constructed of type 317 stainless steel and equipped with a turbine-type agitator, a condenser, receiver, and steam-jet ejector. Temperature of the boiling solution was maintained between 92° and 100° F., and steam at 2- to 3-pounds-per-square inch gage pressure was used in the jacket.

The average composition of the feed, based on eluates from tests 25, 26, and 27, is given below:

Morphine concentration-----	0.175 wt., %
Specific gravity 30°/15° C. ---	.994
Total solids-----	1.64%
Na ₂ SO ₄ content-----	0.84% (est.)
Solids other than Na ₂ SO ₄ -----	.80% (by dif.)
Isopropyl alcohol-----	3.8% (est.)
Isobutyl alcohol-----	2.7% (est.)

The quantity of sodium sulfate is based upon the amount of sulfuric acid required to adjust the pH of the eluates; 5.0 pounds of 66° Baumé acid were required for 95 gallons of eluate as an average for two tests. None of the eluates was analyzed for alcohol content. The concentrations given above are based upon an estimated holdup of 16 pounds of spent IPA wash for every cubic foot of cation exchanger and upon the composition given previously for the spent IPA wash solution.

In one test where filtration of the eluate through adsorbent cotton was attempted, no difficulty was encountered until near the end of the operation. Material that had collected at the bottom of the tank and that appeared to be either an emulsion or a colloidal solution proved to be unfilterable. Attempts to complete the filtration by other means proved unsuccessful.

Foaming of the boiling solution was encountered in every test and was controlled, but not eliminated, by the occasional addition of octyl alcohol, the quantity approximating 5 milliliters per gallon of feed. In spite of anti-foam agent being used and of the operation being conducted with reasonable care, some entrainment always occurred since the condensates were colored and contained small amounts of morphine. Since no indication of entrainment was found for similar evaporations made in an all-glass, long-tube, natural-circulation evaporator used in the laboratory, it must be concluded that the kettle used in the pilot plant was not properly constructed to prevent entrainment.

Tarry solids became encrusted on the walls of the kettle in every test, especially at the liquid-surface level. If concentration of the eluates was carried sufficiently far, sodium sulfate came out of solution, excessive quantities of tarry solids appeared in the concentrate or remained in the kettle, and a greater loss of morphine was incurred. The encrusted tars were dissolved or loosened by a hot-water rinse followed by scrubbing first with a 5-percent sodium hydroxide solution and then with water or a 1-percent sodium hydroxide solution.

A material balance made over eight tests showed that 98.8 percent of the morphine in solutions fed to the evaporator was present in the concentrated liquor, the filtrates and filter cakes from the kettle rinses, and the condensate. If the solids, mainly tars, that were removed upon filtration of the second rinse (i.e., the 5-percent caustic) are not included, the morphine recovery was 94.6 percent. Commercial morphine refiners have established procedures for processing such tars and presumably at least one-half of the morphine present in these tars would be recovered. Based on this assumption, the overall recovery in the concentration step would be approximately 96.7 percent.

The crude morphine liquors obtained by evaporation were brown and dark in color. Thick sirups were obtained when the solids content was 20 percent or more, and thinner sirups that readily drained from the evaporator were obtained with solids contents of about 15 percent. Upon standing for several weeks the sirups solidified partially or entirely depending upon their solids content.

Recovery by Distillation

Exploratory work on a laboratory scale indicated that a distillation method, which is simpler than the ion-exchange procedure, may give satisfactory recovery of the morphine (15) and may be cheaper than the ion-exchange method. The distillation-recovery method was studied on a larger scale and the crude morphine liquor produced by this method was compared with that recovered by ion exchange. A total of five pilot-plant tests was made.

Equipment.--The distillations were conducted in a copper column, 8-3/8 inches I.D., containing 20 plates with a 6-inch plate spacing, and 3 bubble caps per plate. Vapors leaving the top of the column were passed through a partial condenser which preheated the feed and then into a total condenser with the condensate flowing into a 10-gallon decanter. Heat at the bottom of the column was provided by indirect steam in the shell of a tube and shell-type calandria and by the admission of open steam through a perforated pipe. A bottoms stream was withdrawn from the bottom of the column and in the last 3 tests an overflow leg was used to give a continuous discharge and to maintain a liquid level above the calandria.

In the last two tests, an open 100-gallon jacketed kettle equipped with a top-mounted, propeller-type agitator, was used for cooling the bottoms stream and for separation and extraction of the tars. In earlier tests a trough-type cooler was tried but it did not perform satisfactorily.

A 5-gallon Buchner filter was used for filtering the decanted bottoms stream in some of the tests. All evaporations were conducted in the same 55-gallon jacketed kettle used to concentrate the cation-exchanger eluates.

Experimental procedure.--A diagrammatic flowsheet for the distillation recovery operations is given in Figure 9. Prior to distillation, the slightly alkaline extract liquor was adjusted to a pH of about 6.5 with dilute sulfuric acid.

Extract liquor entered the fifth plate of the distillation column at a rate of 17 to 18-1/2 gallons per hour after being preheated to 150°-162° F. in the partial condenser.

IBA in the extract liquor was distilled at atmospheric pressure as the IBA-water azeotrope. The two layers formed upon condensation of the vapors were separated in the decanter and the water layer was pumped directly back onto the fifth plate of the column. This cold-water layer provided the water required for formation of the azeotrope and also created some reflux within the column. The alcohol layer, which was cloudy in appearance upon leaving the decanter, was collected in 55-gallon drums. Small quantities of water separated from the alcohol during the next day or so.

Steam at 15 to 45 pounds per square inch gage was used in the calandria and the quantity of open steam at the bottom of the column was sufficient to produce about 1 pound of bottoms stream for every 2 to 4 pounds of extract liquor fed to the column. Alkaloids and other solubles present in the extract liquor were transferred to this bottoms stream. Dilution of the stream was controlled by adjusting the ratio of direct-to-indirect steam as required.

The hot bottoms stream was continuously withdrawn from the distillation column and cooled in the 100-gallon receiving kettle. Upon completion of the distillation, which usually required about 8 hours, liquor remaining in the column was drained and combined with that in the kettle. To obtain an accurate morphine balance for the distillation step, the calandria section of the distillation column was boiled out with 1-percent sodium hydroxide solution to remove accumulated tars. The column was drained, and after the solution was adjusted to a pH of 6.5 with 30 percent sulfuric acid, it was added to the bottoms stream in the 100-gallon kettle. The bottoms stream remained in the 100-gallon kettle overnight to permit most of the tars to settle and the following morning the supernatant liquid was siphoned off. It had a pH of 5.0 to 6.0 in the various tests and a cloudy appearance.

Although the tars obtained in the first three tests had a morphine content of only 1.5 to 3.2 percent, as compared with 10 to 14 percent usually present in tars from the ion-exchange recovery method, it became apparent that this morphine must be recovered. It should be noted that because of the difficulty encountered in analyzing these tarlike materials for their morphine content, the above values must be considered as only approximate. A procedure for extraction of morphine in the tars, first developed on a laboratory scale, was used for the last two runs in the pilot plant. In the last test, No. 28, the second caustic wash, 54 pounds in weight used to remove tars from the bottom chamber of the distillation column, was adjusted with sulfuric acid to a pH of 9.0, transferred to the 100-gallon kettle, and mixed vigorously with approximately 9 pounds of tars that had settled out of the bottoms stream. The temperature was raised to 185° F. and at this temperature and approximately 9.0 pH, the tars became uniformly dispersed. The dispersion, which had turned black in color, was held at this temperature for a few minutes and then 30 percent sulfuric acid was added slowly. Upon passing the neutral point, the color of the solution changed from black to a grayish-brown and the formation of large globules was observed. Acidification was stopped when the pH reached about 4.0. After the mixture had cooled to room temperature and stood overnight, a clear supernatant liquor, pH 3.6, was siphoned off. The tars were subjected to a second extraction by the same procedure, except that 100 pounds of water were used.

The tar extracts and the supernatant liquor from the still bottoms were combined, adjusted to a pH of 6.2 to 6.9, and concentrated about 16-fold by evaporation at 90°-105° F. and a 28-inch vacuum in the 55-gallon jacketed kettle. In two of the tests these solutions were first filtered; however, this filtration proved to be slow and difficult. Upon completion of the evaporation, which required 3 to 6 hours, the crude morphine liquor was drained and the kettle rinsed twice with 12 to 23 gallons of hot water to remove as much of the encrusted solids as possible.

Experimental results.--The distillation column operated very smoothly after a startup procedure was adopted whereby the calandria section was filled with condensed steam before the feed was introduced. After the column reached steady-state operation, temperature readings typical of those given in Table 17 were obtained. The temperature readings indicate that only five plates and the reboiler were required for the desired separation.

Steam requirements for operation of the column were determined for four tests and are given in Table 18. Approximately 0.90 pound of steam per pound of IBA extract was required for the distillation operation.

The recovery of morphine in each step of the five runs made by the distillation-recovery method is given in Table 19. The results indicate that very little morphine was lost or destroyed in the distillation step. In the last two tests, where morphine in the tars was extracted and included as part of the distillation step, a loss of 1.5 percent was incurred.

Some morphine was always lost in adjusting the pH and in filtering the decanted liquor from the bottoms stream as was done in tests 11 and 12. In a laboratory experiment made with the bottoms stream from test 28, a 5.3-percent loss of morphine was experienced in pH adjustment and filtration. When the pH of this stream was lowered from 5.6 to 4.0, the colloidal solids became flocculated and could be filtered off more readily.

Recovery of morphine in the evaporation step was variable. The low recovery in test 12 presumably was due to the feed being at a pH of 4.5. Fewer solids became encrusted on the evaporator walls when the feed was filtered, but the best recovery was obtained in those tests where the evaporator feed was adjusted to a pH of 6.0 to 6.5. Although little or no foaming was observed, considerable entrainment of morphine again occurred during the evaporation step as in the ion-exchange recovery method.

The crude morphine liquor was concentrated to a solids content of 61 to 84 percent in the first three tests which is higher than is believed possible for the ion-exchange product. In the last two tests, it was concentrated to a solids content of 35 and 22 percent.

The overall loss of IBA in the distillation recovery method was held to 2 to 4 percent in the tests where reasonable precautions were taken to minimize the loss.

In tests 15 and 28 most of the tars were collected. They constituted 0.73 and 0.83 percent of the extract liquor, respectively.

E. Product Evaluation

Typical samples of crude morphine liquors produced by each method were submitted to the Mallinckrodt Chemical Works for determination of their acceptability for production of the pure alkaloids, morphine and codeine. The ion-exchange product, prepared in test 26, was a liquid containing some solids and was obtained by concentrating the cation eluate and the tar extracts. The distillation product was produced in test 28 and it also contained some solids. The analyses of these samples are compiled in Table 20.

Upon completion of their evaluation, Dr. A. H. Homeyer, Associate Director of Research for the Mallinckrodt Chemical Works (11), wrote as follows:

"We have not done enough work on these materials to thoroughly evaluate them from the point of view of plant processing, but on the basis of laboratory examination so far we feel that either 'crude product A' (ion-exchange product) or 'crude product B' (distillation product) could be used. The former appears to be somewhat purer but the latter is more concentrated. We think that a choice would have to be made between them on the basis of economy of processing up to this point. Further processing would be expedited if more concentrated solutions could be prepared."

Samples of products prepared by each recovery method but by less completely developed techniques were evaluated also by Merck and Company, Inc. Dr. W. E. Clapham, Narcotics Products Manager (5), made the following statement:

"We are pleased to report that we were successful in recovering in the laboratory morphine alkaloid, codeine, thebaine, papaverine, and narcotine from each of your crude products. Our yields of morphine were, of course, higher from crude A^{5/} than from crude B^{6/} whereas we

^{5/} Crude A was prepared in the laboratory by ion-exchange adsorption, concentration of eluate, and precipitation of morphine. Crude A was a solid containing 62.0 percent morphine by Matchett and Levine method of analysis.

^{6/} Crude B was prepared in the pilot plant by the distillation-recovery method and contained 13.5 percent morphine by the Matchett and Levine analysis.

obtained higher yields of the other alkaloids from crude B.

"It is our conclusion that we would be able to use either of these crudes in our narcotic manufacturing operations in an emergency although we feel that further process development work will be necessary. This development work could be completed during the period the necessary poppy straw is being grown. Since scientific advancements between now and the date of such an emergency may make obsolete our present methods and the use of present narcotics we do not feel that further development work can be justified at this time."

The proportion of morphine recovered by either refiner is not known, but we believe that any commercially feasible refining process must always recover more than 90 percent of the morphine present in the raw material.

Significant quantities of codeine were present in both products. Since the market value of anhydrous codeine is slightly higher than that of morphine, the sum worth of both must be considered in evaluating the worth of each product.

F. Solvent Recovery

Meal Desolventizing Study

For design calculations, data on the moisture and volatile content of poppy meal at the end of the constant-rate-desolventizing period were obtained experimentally. The loss in weight with time was noted as 50 grams of moisture-free meal wetted with equal weights of IBA and water was electrically heated in a vented container. From these data the resultant plot of drying-rate curves is shown in Figure 10.

The solvent vaporized rapidly during the constant-rate period (section BC of the curve) at a temperature 0° to 15° F. above the boiling point of the IBA-water-azeotrope (b.p. = 194° F.). The constant-rate period ended at about 210° F. In the falling-rate period (section CD), the temperature rose rapidly to about 250° F. and the resultant desolventized meal contained less than 5 percent moisture and volatile matter. The critical moisture and volatile matter content was 0.13 gram per gram of dry solids in one test and 0.11 in the other. These data indicate that most of the IBA evaporates as the azeotrope and, since the azeotrope removes 1 pound of water for every 2 pounds of IBA, the residual moisture and volatile matter should consist largely of water.

A tray-type desolventizer was used in the pilot-plant operations, but no attempt was made to study the desolventizing step.

IPA-IBA-H₂O Solubility Diagram

Data were obtained experimentally with commercial grades of IPA and IBA by a method similar to that described by Othmer (22). The solubility of IBA in water and of water in IBA given by Seidell were used (27). The resultant solubility curve and several tie lines are shown in Figure 11 with the overall composition of the tie-line mixtures indicated by the triangles.

G. Summary of Experimental Results

Storage tests indicated no loss of morphine need be expected over a 24-month period as long as the straw or meal is kept dry.

A satisfactory 4-step, size-reduction procedure employing roller mills and sifters for each step was developed for separation of stems and seed from the crude poppy straw and for grinding the capsular material to pass a 20-mesh sieve. A major portion of the stems was removed in the first step with a simultaneous reduction of about 50 percent in the volume of the straw to be stored. Approximately 6 percent of morphine contained in the crude straw was lost in the discarded stems. Weight of straw to be extracted was reduced by about 30 percent by removal of the stems and seed and at the same time the morphine concentration in the poppy meal was increased from approximately 0.5 to 0.7 percent.

The poppy meal was wetted with extract liquor prior to the extraction step to minimize the quantity of "fines" and was treated with ammonia to release alkaloids from their naturally occurring salts within the plant material. A high ratio of 6.7 pounds of solvent to 1 pound of meal was employed for the extraction step because the extracted residue retained an abnormally large amount of liquor. With a continuous counter-current extractor of the partial immersion type and with water-saturated isobutanol used as the extraction solvent, over 95 percent of the morphine was extracted. The data also indicate that comparable proportions of codeine and thebaine were extracted.

Part of the entrained liquor was removed from the extracted solids by a continuous dewatering press. This liquor was returned to the extractor as a secondary solvent thus permitting a reduction in the primary solvent feed rate by an equivalent amount without any loss in extraction efficiency.

Fines present in the extract liquor constituted 2-1/4 percent of the meal entering the extractor but they were easily removed by a simple filtration.

Laboratory tests indicated that percolation-type extractors cannot handle the meal satisfactorily, the centrifugal extraction system would require some modification, and the filtration-extraction system should handle the meal quite readily and possibly give adequate extraction at a lower solvent ratio.

Two methods were developed for the recovery of morphine from the IBA extract of poppy meal, both of which are considered suitable for commercial operations. The final product was a liquid concentrate containing about 2 percent morphine and 0.3 percent codeine by a commercial refiner's assay. This concentrate can be used as a domestic raw material for morphine production.

In the ion-exchange recovery method, morphine and codeine were adsorbed from the IBA extract by a cation exchanger of low cross-linkage (Duolite C-10) in the hydrogen form. The IBA effluent was passed through an anion exchanger (Duolite A-7) to remove free acids before the alcohol was recycled for extraction of alkaloids from more poppy meal. Alkaloids adsorbed by the cation exchanger were eluted by a 4-percent solution of sodium hydroxide. The eluate was neutralized and concentrated by vacuum evaporation to give a crude morphine liquor. It was necessary to employ an IPA wash to remove tars deposited on the cation exchanger during the adsorption step.

In the distillation recovery method, an IBA-water azeotrope was fractionally distilled from the IBA extract while the alkaloids and other solids were transferred to an aqueous phase. Tarlike solids were separated from the aqueous solution by settling and treated twice with alkali solution and acid to recover much of the occluded morphine. The aqueous solution and extracts were filtered and concentrated by vacuum evaporation.

IV. DESCRIPTION OF THE RECOMMENDED PROCESS

Preliminary design calculations were made for a commercial-size poppy-processing plant. Estimates of the required capital investment; operating costs; type and size of equipment; and requirements for raw materials, supplies, labor, utilities, etc., are given in Tables 21-31. Quantitative flowsheets for the commercial plant are shown in Figures 12-14. Material balances and some basic data used in the design calculations can be found in Tables 32-45.

A. Basis for Selection

Of the two methods developed for recovery of morphine and other alkaloids from the extract liquor, the ion-exchange method was chosen because a cost study indicated that this method would have a lower production cost than the distillation-recovery method.

B. Brief Description of Process

The 11 principal steps in the recommended process are:

1. Enrichment of the capsular material by removal from the crude straw of poppy seed and many stems
2. Storage of the resultant partially ground straw
3. Conversion of the partially ground straw into a meal by grinding and sifting
4. Prewetting of the meal with an IBA extract and treatment with ammonia to convert the morphine and other alkaloids to the alcohol-soluble free-base form
5. Extraction of the treated meal in a countercurrent extractor with water-saturated IBA containing a small amount of IPA
6. Transferral of morphine and other alkaloids from the extract liquor to a cation exchanger
7. Removal of tars deposited on the cation exchanger by use of an IPA wash
8. Elution of alkaloids from the cation exchanger with an aqueous caustic soda solution
9. Neutralization of the cation eluate and concentration by vacuum evaporation to produce crude morphine liquor
10. Recovery and purification of the IBA and IPA
11. Disposal of the desolventized meal and of stems and seed separated from the crude poppy straw.

Sufficient crude poppy straw for a year's operation of the poppy-processing plant must be procured and placed in storage during the harvest season which will not exceed 3 weeks in length. The crude straw presumably will be delivered to the plant in motor trucks. After the straw is dumped, it is transferred by inclined suspended-flight conveyors to an asphalt-paved storage area which can hold a 12-hour supply of straw for the first-break operations. Two tractors with wooden pusher blades push the material into two recessed screw conveyors for transfer of straw into the straw-processing building. Ten cut-hay feeders (Figure 12) control the feed rate to five double-roller mills equipped with Lepage corrugated rolls. Tramp iron is removed ahead of each mill by a magnetic separator. The crushed straw is separated by two sets of double-screen scalpels into three fractions; namely, partially ground straw, stems, and a seed-bearing fraction.

The seed-bearing fraction is transported by motor truck and dumped into the hopper of a portable screw conveyor for proper placement within a prefabricated steel storage building. The stems are chopped and conveyed pneumatically to an asphalt-paved surface where they are stored outdoors until they are withdrawn for use as fuel. The partially ground straw is pneumatically conveyed to one of six prefabricated steel buildings and placed in storage. The first-break milling operation and related operations are performed 24 hours per day for 18 days during the harvest season.

The remainder of the poppy-processing plant will operate 24 hours per day, 300 days per year. For subsequent milling operations, a day's run bin is filled daily with partially ground straw taken out of storage by the pneumatic conveying system which is operated under vacuum. As the straw is processed through the second, third, and fourth breaks, as shown in Figure 12, more stems are removed. These stems are conveyed directly to the boiler house and burned as fuel in the furnace of the steam boiler. The seed-bearing fraction is also removed from storage, transported by motor truck to the straw-processing building, and elevated into a day's run bin. A seed cleaner separates this fraction into clean seed, which is returned by truck to storage for eventual sale, and a meal fraction which is blended at the specified rate with the minus 20-mesh meal from the second, third, and fourth breaks.

The resultant poppy meal accumulates in a day's run bin ahead of the extractor (Figure 13). This meal is fed by a gravimetric feeder into a mixing and reaction conveyor. Gaseous ammonia and water are added to a stream of filtered extract liquor as it is pumped through an injector-type mixer, and the resultant wetting liquor is mixed with poppy meal in the proportions specified in Figure 13 in a paddle-type conveyor. The wetted meal is held in the mixing and reaction conveyor for 30 minutes and then enters the Kennedy extractor at stage 1.

The meal is extracted for 45 minutes at 140° F. and passes through 20 extraction stages. Solvent A, a water-saturated solution of IBA containing a small amount of IPA, enters at stage 20; and solvent B (i.e., press liquor) is introduced between stages 16 and 17. (Provision should be made in the design of the extractor to permit this location to be changed later if found desirable.) Both solvents are preheated to 135°-140° F. and flow controllers are used to maintain constant flow rates. Since the flow of solvent B is dependent upon the amount of liquor squeezed out of the extracted solids, adjustments are made in the A rate to maintain an overall ratio of 6.7 pounds of solvent to 1 pound of meal.

The extracted meal goes directly to a continuous dewatering press equipped with a vapor-tight housing. The pressed meal is broken up in a paddle conveyor and passes through a rotary airlock feeder valve into the side opening of a venturi tube in the flash-desolventizer duct. A superheated vapor stream containing a mixture of IBA, IPA, and water vapors picks up the solids and transports them through the 24-inch desolventizing duct to the cyclone collector where the desolventized meal is discharged through another rotary valve and then transported by screw conveyors to the boiler house to be burned as fuel. Vapors leave the cyclone at 350° F. to a turboblower, pass through a superheater where they are reheated to 550° F. with Dowtherm vapor at 700° F., and are recycled to the desolventizing dust. A quantity of vapors equal to that produced by vaporization of the solvent in the feed is withdrawn from the recycle stream. These hot vapors pass through a set of dust separators and recovered dust is added to the desolventized meal. The condensate from these vapors is separated in a decanter into two layers--the alcohol layer is returned to the solvent A work tank and the water layer is sent to distillation column No. 3 for recovery of the dissolved alcohols.

Fines are removed from the extract liquor by pumping it through one of two enclosed rotating-leaf pressure filters at an average rate of 15.6 gallons per hour per square foot of filtering area. The filtration period for each filter is 2 hours. The washed filter cake is transferred by screw conveyors to the flash desolventizer for solvent recovery.

To insure a clear feed to the ion-exchange columns, filtrate from the rotating-leaf filters is cooled to 100° F., mixed with filter aid, and filtered through either of two precoated, plate-and-frame filter presses at an average rate of 8 gallons per hour per square foot of filter area. Each press filters liquor for an 8-hour period before the flow is diverted to the other press.

Three cation-exchange columns, each filled with a 5-foot bed of Duolite C-10 resin, are used for adsorption of the morphine and other alkaloids from the extract liquor. Liquor is pumped through one of the columns by downflow at a rate of 36 gallons per hour per square foot and the effluent flows directly to one of two anion columns, each containing a 3.9-foot bed of Duolite A-7 anion resin. Effluent from the anion column is returned directly to the solvent A work tank.

Next, for removal of tars, 417 gallons of IPA, 91 volume percent, are pumped into the cation column by upflow at a high rate, aerated for 10 minutes, and then drained and fed to the IPA-wash evaporators. To elute the alkaloids, 700 gallons of a 4-percent sodium hydroxide solution are pumped in at a similar high rate and aerated for 10 minutes; the walls of the column are washed with a water spray, the bed washed with 2,350 gallons of rinse water, and the column drained to the eluate neutralization tanks. The exchanger is regenerated with 700 gallons of 5-percent sulfuric acid solution, aerated as before, and washed with 2,050 gallons of demineralized water to bring the water effluent up to a pH of about 3.5. The resin is left covered with water, which is displaced during the "sweetening on" step of the next cycle.

Acids present in the alcohol effluent of the cation column are adsorbed in the anion column. The anion exchanger is regenerated with 163 gallons of 1-percent sodium hydroxide solution, aerated, and rinsed with 940 gallons of demineralized water to a pH of about 9.0. The first two-thirds of the regenerant effluent are sent to distillation column No. 3 for alcohol recovery and the remaining one-third is discarded.

The exhaustion period for each set of columns will be 10 hours when the resin is new. Through continued use, the capacity of the resin will decrease to 60 percent of its initial value and the resultant cycle will be 6 hours long. The time allotted for the various steps in a complete cycle for each column is shown below:

<u>Time interval -- hours</u>				
<u>Operating step</u>	<u>Cation column</u>		<u>Anion column</u>	
	<u>Spent resin</u>	<u>New resin</u>	<u>Spent resin</u>	<u>New resin</u>
Sweetening on-----	0.46	0.46	0.18	0.18
Exhaustion-----	1.54	2.87	2.82	4.82
Drainage-----	0.33	0.33	0.47	0.47
IPA wash and drainage----	.52	.52	----	----
Elution and drainage----	1.52	1.52	----	----
Regeneration-----	0.90	0.90	1.56	1.56
Idle time-----	<u>.73</u>	<u>3.40</u>	<u>0.97</u>	<u>2.97</u>
Total length of cycle--	6.00	10.00	6.00	10.00

To avoid loss of morphine, the cation eluate is neutralized as soon as possible with 50 percent sulfuric acid to a pH of 6.9. The neutralized eluate is concentrated fivefold in a long tube, vertical evaporator, and then 3.5-fold in an agitated, falling-film evaporator (Figure 14). Both evaporators are operated under 28.1-inch Hg. vacuum and steam at a pressure of 2- to 3-pounds-per-square inch gage is used in the steam chest to avoid overheating the solution and incurring a loss of morphine. The product, crude morphine liquor, is pumped to 10,000-gallon storage tanks and held there for shipment to the morphine refiner. Vapors from the agitated falling-film evaporator are condensed and sent to storage for use as process water.

Solvent vapors present in vent gases from all process equipment, except the above two evaporators, are adsorbed in a pair of carbon adsorbers which operate at atmospheric pressure and on an 8-hour cycle--4 hours for adsorption of solvent vapors, 2 hours for desorption of the carbon by steaming, and 2 hours for cooling and idle time. Solvent vapors from the cation-eluate evaporators are adsorbed in another pair of carbon adsorbers operating under 28-29 inches Hg. vacuum and an 8-hour cycle.

The remainder of the solvent-recovery apparatus consists of a long tube vertical evaporator, two pot evaporators which are used to concentrate the spent IPA wash, and three distillation columns for recovery and separation of the IBA and IPA present in various aqueous streams. All of this equipment is operated at atmospheric pressure.

The feed to distillation column No. 1 is composed of condensate from the first cation-eluate evaporator and condensates from the two-carbon adsorption systems. The feed at 70° F. is pumped onto the 15th plate in the column and both the IBA and IPA are distilled overhead at compositions closely approaching those of their respective water azeotropes. The column is operated with an 0.8 to 1 reflux ratio. The bottoms discharged from this column are essentially free of both alcohols and after being cooled to 100° F. they are sent to a storage tank for subsequent use in operations requiring treated water.

The feed to distillation column No. 2 is a partially vaporized mixture consisting of vapors from the IPA wash evaporators, the cold condensate from distillation column No. 1, and a small amount of water as required to satisfy the alcohol-water azeotropes. The feed enters on the 25th plate and is separated into (1) a distillate containing 0.90 mole fraction IPA-H₂O azeotrope and 0.10 mole fraction IBA-H₂O azeotrope and (2) a bottoms stream containing 0.95 mole fraction of the higher boiling azeotrope and 0.05 mole fraction of the lower. Separation of these two alcohol-water azeotropes is a difficult operation and the compositions given for the distillate and the bottoms are the best considered practical. The distillate is condensed, cooled to 100° F., and sent directly to the 91-percent-IPA work tank. The bottoms are combined with the distillate from column No. 3, cooled to 100° F., and separated in a decanter into two layers--a water layer which is fed to column No. 1 and an alcohol layer which is returned to the solvent A work tank. This alcohol layer contains about 75 percent IBA, 6 percent IPA, and the remainder water. Distillation column No. 2 contains 50 bubble-cap trays and is operated with a 6.6 to 1 reflux ratio.

For distillation column No. 3, the feed consists of the first two-thirds of the spent anion regenerant solution and the water layer from the flash-desolventizer condensate. This column is packed with Raschig rings and the cold feed enters at the top of the packed section. The bottoms are a stream of water essentially stripped of both alcohols and the distillate is composed largely of the IBA-water azeotrope with a small proportion of the IPA-water azeotrope.

No equipment has been included for recovery of the small amount of alkaloids present in the spent IPA wash from the cation exchanger. These alkaloids presumably can be recovered, but the decision whether to do so can best be made after some material accumulated from the commercial operation has been examined and evaluated.

V. ANALYSIS OF RECOMMENDED PROCESS

A. Yields

The following yields or recoveries are anticipated in the commercial operations:

1. From 100 pounds of poppy straw, 69 pounds of poppy meal are obtained, together with 6.5 pounds of poppy seed. The morphine concentration in the meal should be approximately 0.5 percent by a commercial refiner's assay method.

2. In the extraction step, 95 percent of the morphine is extracted and transferred to the IBA extract.

3. In the ion-exchange operations, 98 percent of the morphine is adsorbed by the cation exchanger, and 95.5 of that adsorbed is eluted by the sodium hydroxide solution.

4. In the evaporation step, the morphine recovery is 96.7 percent.

The overall recovery to this point, based upon morphine present in the poppy meal, is 86.0 percent. In purification of the crude morphine liquor into medicinal-grade morphine at the refinery, a recovery of 90 percent is assumed. Thus, for the daily production of 200 pounds of refined anhydrous morphine, the crude morphine liquor must contain 222 pounds of the anhydrous alkaloid. This liquor also contains about 37 pounds of anhydrous codeine.

B. Estimated Costs

Even with mechanized production methods, domestically grown poppy straw is too expensive to be economically feasible as a source for crude morphine liquor except during a national emergency when imported opium may be unavailable.

For this cost estimate it is assumed that the poppy-processing plant will be a new and independent factory erected in the rural area where the poppies are grown. If advantage can be taken of service or supporting facilities already installed at an existing plant, the investment in the poppy-processing plant could be reduced accordingly. In order to produce 60,000 pounds of medicinal-grade morphine annually, it was calculated that the crude morphine liquor shipped to the refiner must contain 66,670 pounds of anhydrous morphine.

The fixed capital costs required for this plant totalling \$3,766,000 (1958 basis) are shown in Tables 22-25 and 31. This is equivalent to an investment of \$57 per pound of anhydrous morphine produced annually.

The estimated production cost is \$10.25 per ounce of anhydrous morphine present in the crude morphine liquor, which includes a charge of \$10.24 for the crude poppy straw; \$1.01 for the cost of other raw materials, labor, supervision, utilities, supplies, maintenance, and fixed charges other than taxes and insurance; and a credit of \$1.00 for byproduct codeine (calculated at a value of \$6.00 per ounce). To this cost must be added other overhead expenses such as administrative costs, social security, and other indirect wage payments; selling costs; income taxes; and profits. Tables 26-30 list the costs included for raw materials, supplies, utilities, maintenance, fixed charges, labor, and supervision.

Since the current market price for refined morphine (anhydrous basis) is \$12.40-12.70 per ounce (December 1959), the proposed process will not be economically competitive with current production from opium from which the morphine can be obtained at a much lower unit-cost than from the poppy straw. Cost of the crude poppy straw is estimated at \$1,000 per ton (24). This figure is based upon a yield of 600 pounds of the straw per acre of irrigated land and upon a gross return to the farmer of \$300 per acre for growing, harvesting, and delivering the straw to a receiving station or processing plant 10 miles distant. Because a large portion of the production cost of the crude morphine liquor is accounted for in charges for the crude straw (see Table 21), any significant change in straw cost or morphine content will have considerable influence on cost of the morphine.

The costs of raw materials, chemicals, supplies, utilities, labor, and the crude poppy straw were estimated for early 1959.

Mention should also be made of the capital that must be available to purchase the 10,910 tons of crude poppy straw required for a year's operation. As is common with many agricultural commodities, only one crop is harvested annually, and in this case the entire crop will be delivered during a 3 weeks' period. At a price of \$1,000 per ton, the straw will cost almost \$11 million.

C. Byproducts

Operation of the processing plant will also produce,
in addition to morphine and codeine, the following
byproducts:

	<u>Unit value</u>	<u>Quantity per day</u>	<u>Quantity per pound of an- hydrous morphine</u>
		<u>Pounds</u>	<u>Pounds</u>
Poppy seed-----	Nominal	4,728	21.3
Desolventized meal and stems from second, third, and fourth breaks-----	Do.	51,000	229.7
Stems from first break-----	Do.	11,600	52.3

The amount of fuel oil needed for producing steam may be reduced approximately one-third by burning the desolventized meal and the stems in the furnace of the boiler. Such usage will also eliminate a waste-disposal problem. The poppy seed may be sold to an oil mill for the production of oil and meal, but no monetary return has been included in the present estimate.

D. Possible Process Improvements

In the course of the investigation and the preparation of this report various possibilities for improving the process have become apparent but for various reasons they have not been explored.

The introduction of IPA into the process and the necessity for purifying the two alcohols (IPA and IBA) complicate the design and operation of the processing plant and add to the cost. If an organic solvent must be employed for extraction of the alkaloids, then serious consideration should be given to use of IPA as the sole solvent. Mehlretter and Weakley's laboratory investigation (20) at the Northern Laboratory indicated that IPA containing about 12 percent water may be a satisfactory extraction solvent. If an IPA concentration higher than 91 volume percent, the azeotropic composition, should be needed to remove tars from the cation exchanger, equipment to accomplish this purification could readily be designed and installed.

The use of hexane rather than IPA to remove tars from the cation exchanger may prove more satisfactory since it should be a better solvent for the tars. This solvent forms an azeotrope with either IPA or IBA but should be more readily separated by distillation than the IPA-IBA mixture. Also, if recovery of alkaloids from these tars is warranted, the alkaloids probably can be extracted from the hexane wash with either IBA or IPA containing the proper amount of water. However, the use of a mixed solvent system is not desirable.

Research studies, conducted on a limited scale in the laboratory after most of the developmental work was completed, indicated the possibility of developing a process using water as a solvent for extraction of alkaloids from the poppy meal and ion exchange as a means of separating alkaloids from the aqueous extract. The economic advantage of using water rather than IBA as the extraction solvent, and the greater simplicity of the overall resultant process make it attractive. The results obtained in this investigation are described by McGuire, et al. (18).

If the experimental work could have been continued, the distillation recovery process, which is simpler and uses less equipment, might have been developed to give the lower production cost. Morphine recovery by this process was comparable to that for the ion-exchange method, 85.1 versus 86.0 percent (design values), based on the Matchett and Levine analyses. However, because the distillation product showed a proportionally greater decrease in morphine content by the commercial refiner's assay, the corrected yield from a ton of poppy meal was appreciably lower, namely 119 ounces as compared with 145 ounces by

the ion-exchange process. No explanation can be given for the variation in the morphine assays of the two products. The yield for the distillation method might be improved by distilling the IBA-water azeotrope under vacuum rather than at atmospheric pressure, and by the use of organic solvents rather than alkali and acid to dissolve the tars and recover the alkaloids present in them.

E. Evaluation of Recommended Process

All of the operations but one, in the recommended process, may be considered either as standard for the chemical and grain-milling industries or as minor modifications. The one exception is selection of a flash desolventizer for removal of solvent present in the extracted, pressed meal. The principle involved in the flash desolventizer is essentially the same as that in pneumatic conveying dryers, and a number of these have been in successful use for a number of years therefore no unusual difficulties are anticipated.

As far as possible, all process operations are continuous rather than intermittent or of the batch type. The exceptions are filtration of the extract liquor, the ion-exchange operations, the recovery of solvent vapors from vent gases, and certain evaporation operations. Operations of this type often are conducted on an intermittent basis with continuous flow being obtained by the use of multiple units.

All of the equipment is of conventional type and a very large portion is of iron and steel construction. For the ion-exchange equipment some Koroseal-lined columns, rubber-lined tanks, Uscolite piping, and Worthtite pumps are required; in the evaporators for concentrating the cation eluate some stainless steel, type 304, is specified but none of these materials is normally considered difficult to procure. Thus, the process equipment can be designed, purchased, and fabricated with a minimum of delay, if so desired.

All of the operations are routine in nature and none with the possible exception of the ion-exchange step will require the use of highly skilled help. While the operators should be intelligent, alert, and diligent, a large majority of the operations are comparatively simple and the operators should readily discharge their duties after a comparatively short training period. Since only the ion-exchange operations presumably will require technical supervision on each shift, it will be possible to operate the plant with a minimum of technical personnel.

Water requirements for the poppy-processing plant are moderate. Most of the water will be used for cooling purposes and if an adequate supply (3.2 million gallons per day) is available at 76° F., the installation and operation of a cooling tower will not be necessary. The essentially pure water required for the ion-exchange operations will be furnished by a demineralized water system.

None of the waste water streams will require purification, thus disposal of sewage will not be a problem nor a determining factor in locating the plant.

The cost of producing the crude morphine liquor exclusive of charges for the crude poppy straw is only \$1.01 per ounce of morphine. Since the straw is expensive, any agronomic improvements that either increase the yield of poppy capsules or increase their morphine content will significantly reduce the cost of the crude morphine liquor. Similarly, any deterioration will increase the cost.

Although the liquor is not as rich in morphine and associated alkaloids as is opium, its characteristics are such that the refiner should be able to process the liquor without making extensive modifications to his present refining process.

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Mention of firm names or proprietary products is made solely for information and to explain the exact experimental conditions; it does not imply endorsement of such firms or products over other firms engaged in similar business or over products of similar nature not mentioned.

VII. PUBLICATIONS AND PATENTS

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INTRODUCTORY STATEMENT FOR DESIGN CALCULATIONS

As a basis for the design calculations used to establish the size of various pieces of process equipment, material balances were prepared for the principal steps of the recommended process. These are detailed in Tables 36 through 47.

The size and composition of process streams are based on average values obtained from pilot-plant investigations. In some material balances the weight of each stream per 100 pounds of poppy meal fed to the extractor was used. From weights of the process streams and their composition such component quantities as water, ammonia, isobutanol, total solids, and morphine were calculated. In several instances suppositions were made where data were unavailable or the composition obviously was incorrect. Total weight of the process stream is the sum of weights given for the various components excluding morphine.

In material balances except those for the distillation system, the presence of isopropyl alcohol is ignored. No attempt was made to recover this alcohol during the developmental work. It is realized that in commercial operations, isopropyl alcohol inevitably will appear in any process stream where isobutanol is present. Purity of the streams depends upon the ultimate separation of isopropanol and isobutanol during the distillation step. Limits set for this separation are considered the best that can be expected. If isopropanol is equally as good as, or is better than, isobutanol as an

extraction solvent, further work may show that a less rigorous separation is desirable or that only isopropyl alcohol, plus an appropriate amount of water, need be used.

As a prerequisite to calculating material balances, it was necessary, based upon experimental data, to estimate the percentage of morphine recovered in each step of the commercial process. These values are given in Table 34.

Another prerequisite was to calculate the quantity of morphine that must be present in certain process streams. These calculations are shown in Table 35.

All values of morphine in Tables 34-47, inclusive, are based on the Matchett and Levine method of analysis unless stated otherwise. The letter "M" in quotation marks is used as a symbol for morphine.

TABLE 1.--Milling conditions used at Allis-Chalmers

Break	Type of roll	Arrange- ment	Clear- ance	Fast roll	Slow roll	Feed rate	Total feed to rolls
			In.	R.p.m.	R.p.m.	Lb. min.	Lb.
No. 1-	LePage corrug., 5/in.	-----	0.028	515	409	10	17
No. 2-	Conventional spiral cut corrug., 12/in.	Dull-to- dull	.010	585	402	3	7.5
No. 3-	Conventional spiral cut corrug., 16/in.	do.	.003	585	390	1.5	6.6
No. 4-	Conventional spiral cut corrug., 22/in.	Sharp- to- sharp	.002	515	206	1	3.0

TABLE 2.--Product obtained from each break
at Allis-Chalmers

Break	: Proportion of product obtained		
	: Based on : : material : : fed to : : each : : break :	: Based : : on : : crude : : straw :	: Based : : on : : product :
	: <u>Percent</u> :	: <u>Percent</u> :	: <u>Percent</u> :
No. 1-----	: ---- :	: ---- :	: ---- :
No. 2-----	: 30.7 :	: 13.5 :	: 23.4 :
No. 3-----	: 59.8 :	: 23.2 :	: 40.0 :
No. 4-----	: 86.5 :	: 18.8 :	: 32.5 :
No. 4, re- : tained on :	: : :	: : :	: : :
20-mesh--	: 10.8 :	: <u>2.4</u> :	: <u>4.1</u> :
Total--	: ---- :	: 57.9 :	: 100.0 :

TABLE 3.--Material balance for preparation at NU of poppy meal, lot MS-7

Fraction	Break				Abbe mill	Seed separa- ation	Total weight of fraction	Proportion of crude straw
	No. 1	No. 2	No. 3	No. 4				
	Pounds	Pounds	Pounds	Pounds	Pounds	Pounds	Pounds	Percent
<u>Material in:</u>								
Stock to break-----	4,275	2,760.9	2,100.1	1,148.9	403.2	814.0	4,275	100
<u>Material out:</u>								
Stock to next break---	2,760.9	2,100.1	1,148.9	403.2				-----
Stems-----	677.0	75.2	53.6	110.7			916.5	21.8
Meal-----	-----	575.0	828.6	643.7	398.7	487.4	2,933.4	69.0
Seed-bearing fraction-	814.0	-----	-----	-----	-----	-----	-----	-----
Seed-----						279.0	279.0	6.5
Sweepings-----	15.0	None	None	15.3	None	None	30.3	(1/)
Total out-----	4,266.9	2,750.3	2,031.1	1,1172.9	398.7	766.4	4,159.2	
Loss: By difference----	8.1	10.6	69.0	2/-24.0	4.5	47.6	115.8	<u>2.7</u>
							100.0	

1/ Proportion represented by sweepings arbitrarily has been divided almost equally between stems and meals.

2/ This gain in weight is due, in part, to the sweepings that accumulated during break Nos. 2, 3, and 4.

TABLE 4.--Sieve analysis of poppy meal

<u>Screen size</u>	<u>Average cumulative</u>
<u>U. S. standard</u>	<u>percent retained</u>
No. 10-----	0.2
No. 20-----	4.3
No. 40-----	46.9
No. 60-----	71.2
No. 80-----	80.4
No. 100-----	87.8
No. 200-----	95.3
Pan-----	99.9

TABLE 5.--Bulk density of crude poppy straw and of
various straw and meal fractions

Material	Bulk density Lb./cu. ft.
Crude poppy straw-----	6.0
Stems from first, second, and third breaks-----	2.4-3.0
Stems from fourth break-----	5.5
Partially ground straw, loose,-----	6.7
slightly packed,-----	8.8
tamped-----	9.5
Seed-bearing fraction-----	12.9
Poppy meal (9% M. and V. M.)-----	12.5-13.0
Pressed meal (60% M. and V. M.) ^{1/} ----	20.5
Wetted poppy meal (66% M. and V. M.) ^{1/} -----	24.0
Rotary filter cake (74% M. and V. M.) ^{1/} -----	31.8
Extracted meal (80% M. and V. M.) ^{1/} --	49.3

^{1/} Measurements were made on poppy meal wetted
with extract liquor to the specified M. and V. M., i.e.,
moisture and volatile matter content.

TABLE 6.--Morphine content of stems and poppy meal

Fraction	Morphine content	Weight of fraction	Morphine in fraction
	<u>Percent</u>	<u>Pounds</u>	<u>Pounds</u>
Stems from first break-----	0.13	677.0	0.880
Stems from second break-----	.10	75.2	.075
Stems from third break-----	.10	53.6	.054
Stems from fourth break-----	.18	110.7	.199
Poppy meal-----	.68	2,933.4	19.947
			<u>21.155</u>
Morphine lost in discarded stems = (0.880 - 0.075 - 0.054 - 0.199) (100)/21.155 = 5.7 percent.			

TABLE 7.--Typical process conditions and values for solvent
extraction of poppy meal

		:
Meal (air-dry) feed rate, lb./hr.-----		: 12
		:
Wetting liquor, rate, lb./hr.-----		: 20
		:
Solvent A rate, lb./hr.-----		: 54.0
		:
Solvent B rate, lb./hr.-----		: 26.2
		:
Overall solvent ratio-----		: 6.7
		:
Solids retention time within extractor,		:
min.-----		: 45
		:
Extractor temperature, °F.-----		: 140
		:
Solvent feed temperatures, °F.-----		: 135-140
		:
Fines removed from extract liquor,		:
lb./100 lb. poppy meal-----		: 1.75
		:
Proportion of anion effluent in solvent A,		:
%-----		: 45
		:
Anhydrous ammonia rate, lb./100 lb.		:
poppy meal-----		: 1.25
		:

TABLE 8.--Typical analytical values for extraction and pressing operations

Description of sample	Type of sample	Morphine concentration	Specific gravity	pH	Moisture and volatile matter	Total solids	Petroleum ether solubles	Sulfated ash	NH ₃	Water	Iso-butyl alcohol
		%	30°/15° C.	%	%	%	%	%	%	%	%
Poppy meal	Representative	0.67-72	---	---	9-10	---	3/ 0.75	4/ 18.74	---	---	---
Solvent A	do	0.002	0.832	8.2	---	0.40	.39	0.075	0.003	16.3	83.3
Solvent B	do	.009	.827	6.7	---	.86	.51	.032	.002	15.3	83.8
Extract liquor from test period	do	.225	.817	8.2	---	2.06	1.36	.057	.024	6.55	91.4
Extracted meal	Spot	-----	---	---	79.5	---	---	---	---	---	---
Pressed meal	do	-----	---	---	5/ 60.7	---	---	---	---	---	---
Pressed liquor	Representative	.008	.824	6.6	---	0.40-0.88	---	.049	---	12.5	---

1/ pH values as read directly for alcohol solutions.

2/ By difference.

3/ Single sample analyzed.

4/ Single lot of meal analyzed.

5/ From material balance calculations, it was concluded that the preseed meal contained about equal quantities of isobutanol and water.

TABLE 9.--Material balance for extraction of poppy meal

	Components		Total
	Morphine	Solids	stream
	<u>Oz./hr.</u>	<u>Lb./hr.</u>	<u>Lb./hr.</u>
<u>Material in:</u>			
Solvent A-----	0.018	0.22	54.0
Solvent B-----	.036	.23	26.2
Wetted meal----- ^{1/}	<u>2.065</u>	<u>11.31</u>	<u>32.0</u>
Total-----	2.119	11.76	112.2
<u>Material out:</u>			
Extracted meal----- ^{2/}	0.118	11.05	53.9
Extract liquor-----	1.265	0.72	35.1
Wetting liquor-----	0.721	.41	20.0
Fines and entrained liquor----- ^{3/}	<u>.067</u>	<u>.34</u>	<u>1.3</u>
	2.171	12.52	110.3
Material in - material out-----	+0.052	+0.76	-1.9
Difference-----	+2.5%	+6.5%	-1.7%

^{1/} 12.0 pounds poppy meal, 0.70 percent morphine content and 20.0 pounds wetting liquor containing 0.225 percent morphine.

^{2/} Assuming meal, dry-basis, contains 5 percent of morphine in dry feed solids and entrained liquor contains 0.008 percent morphine.

^{3/} Assuming dry solids contain 0.6 percent morphine and entrained liquor contains 0.225 percent morphine.

TABLE 10.--Morphine extraction efficiency based upon NU's and Mallinckrodt's analyses

Process stream	Quantity	Specific gravity	Morphine concentration:		Morphine content	
			By NU	By MCW ^{1/}	By NU	By MCW
	Pounds	30°/15° C.	Percent	Percent	Ounces	Ounces
Poppy meal-----	151.8	----	0.67	0.451	16.273	10.954
Solvent A-----	647.3	0.83	.0004	-----	0.041	-----
Solvent B-----	306.3	.82	.0063	-----	.309	-----
Extract liquor--	387.8	.82	.223	.155	13.837	9.617
Press liquor----	317 (est.)	.82	.0087	-----	0.441	-----
Morphine extracted = [Morphine in extract and press liquors - (Morphine in solvents A and B)] (100)/(morphine in poppy meal).						
Morphine extracted, by NU analyses =			$(13.837 + 0.441) - (0.041 - 0.309) \times 100 = 85.6\%$			
			16.273			
Morphine extracted, based upon MCW analysis of poppy meal and extract liquor						
= $(9.617 + 0.441) - (0.041 + 0.309) \times 100 = 88.6\%$						
			10.954			

^{1/} Courtesy of A. H. Homeyer and G. L. DeLaMater (11).

TABLE 11.--Extraction efficiency for codeine
and thebaine^{1/}

Process stream	Codeine		Thebaine	
	<u>%</u>	<u>Oz.</u>	<u>%</u>	<u>Oz.</u>
Poppy meal-----	0.073	1.773	0.034	0.826
Extract liquor----	.024	1.489	.011	.683
Codeine extraction = $(1.489/1.773) 100 = 84.0\%$				
Thebaine extraction = $(0.683/0.826) 100 = 82.7\%$				

^{1/} Courtesy of A. H. Homeyer and G. L.

DeLaMater (11).

TABLE 12.--Typical extraction profile

	<u>Morphine concentration</u>	
	<u>Solids</u>	<u>Liquor</u>
	<u>Percent</u>	<u>Percent</u>
Poppy meal feed, at 8.6% moisture----	0.70	-----
Liquor leaving stage No. 0-----	----	0.221
Solids leaving stage No. 1-----	.46	-----
Material leaving stage No. 2-----	.34	.178
Material leaving stage No. 4-----	.26	.135
Material leaving stage No. 6-----	.20	.092
Material leaving stage No. 8-----	.16	.070
Material leaving stage No. 14-----	.09	.025
Material leaving stage No. 20-----	.04	.008
Solvent A, entering stage No. 20-----	----	.002 ^{1/}
Solvent B, entering stage No. 16/17--	----	.012

^{1/} Ferricyanide method of analysis used.

TABLE 13.--Sieve analysis of fines

<u>Screen size</u>	Cumulative percent
<u>U. S. standard</u>	<u>retained</u>
No. 12-----	0.4
No. 20-----	23.1
No. 40-----	40.2
No. 100-----	48.1
No. 200-----	58.1
No. 325-----	70.0
Pan-----	100.0

TABLE 14.--Adsorption of morphine by cation and anion exchangers

Test No.	Morphine concentration			Morphine content			Morphine adsorbed by cation exchanger		
	Cation : influent	Cation : effluent	%	Cation : influent	Cation : effluent	Anion : effluent	Oz.	Oz./cu. ft.	%
16--	0.181	0.0026	0.0022	25.18	0.35	0.28	24.83	6.21	98.6
17--	.179	.0075	.0070	30.26	1.23	1.02	29.03	7.27	96.0
18--	.191	.0026	.0028	24.51	0.32	0.35	24.16	6.03	98.7
19--	.197	.0059	.0053	24.58	.74	.63	23.84	5.96	97.0
20--	.213	.0118	.0103	24.73	1.41	1.13	23.32	5.82	94.3
21--	.211	-----	.0013	21.34		0.14	21.20	5.29	99.5
22--	.216	-----	.0014	24.98		.15	24.83	6.21	99.3
23--	.218	-----	.0034	25.72		.39	25.33	6.35	98.5
24--	.199	-----	.0025	21.94		.28	21.66	5.43	98.7
25--	.205	-----	.0043	22.39		.49	21.90	5.47	97.8
26--	.204	-----	.0040	22.22		.42	21.80	5.22	98.1
27--	.206	-----	.0014	21.06		.14	20.92	5.71	99.3

TABLE 15.--Data for alcohol washes

Test No.	Alcohol used	Weight of wash collected ^{1/}	Morphine in wash	Total solids in wash	Petroleum ether solubles
		Lb.	Oz.	% Lb.	g ₂ /
21--	Isopropanol 99% by vol.	127.1	0.67	1.09	1.39
22--	Methanol 99.8% by wt.	(1) 103.5	1.12	1.79	1.85
		(2) 96.2	0.38	0.96	0.92
23--	Methanol 99.8% by wt.	(1) 96.0	1.22	1.72	1.65
		(2) 103.0	0.61	0.93	0.96
24--	Methanol 99.8% by wt.	(1) 101.4	1.38	1.67	1.69
		(2) 99.8	0.64	0.87	0.87
25--	Isopropanol 91% by vol.	89.4	.72	1.37	1.22
26--	Isopropanol 91% by vol.	92.5	.79	1.41	1.30
27--	Isopropanol 91% by vol.	94.9	.72	1.19	1.13

^{1/} Two washes were used in tests 22, 23, and 24.

^{2/} Percent of total solids.

TABLE 16.--Morphine content of successive fractions
of eluate, Test 21

Eluate fraction	Vol. of eluate	Morphine content	Cumulative total of morphine eluted
	<u>Gallons</u>	<u>Ounces</u>	<u>Ounces</u>
<u>1</u> / 1----	42.2	22.29	22.29
2----	22.5	0.81	23.10
3----	19.4	.20	23.30
<u>2</u> / 4----	54.8	.41	23.71
5----	18.4	.06	23.77
6----	21.5	.02	23.79

1/ At the beginning of the elution step,
21.8 gallons of 4% NaOH solution had been intro-
duced, as was done in all tests.

2/ After collection of fraction No. 3,
22 gallons of 2% NaOH solution were introduced
into the drained column.

TABLE 17.--Temperature gradient in distillation column

	:	
	:	<u>°F.</u>
	:	
Feed temperature-----	:	150-162
	:	
Column temperatures:	:	
	:	
Bottom chamber-----	:	215
	:	
First, second, and	:	
third plates-----	:	214
	:	
Fourth plate-----	:	208-210
	:	
Fifth plate (feed)--	:	195
	:	
Seventh to twentieth	:	
plates-----	:	195-194
	:	

TABLE 18.--Steam requirements for
distillation operation

Test No.	Steam used ^{1/}		
	Direct	Indirect	Total
11-	0.8	None used	0.8
12-	.34	0.60	.94
15-	.34	.52	.86
28-	.54	.40	.94

^{1/} Pounds of steam used per pound
of extract liquor fed to the column.

TABLE 19.--Morphine recovery by the distillation
recovery method

Test No.	Morphine recovery ^{1/}				Overall ^{2/}
	Distil- lation step	pH adjustment and filtra- tion steps	Evapora- tion step		
	Percent	Percent	Percent		Percent
Prel. ^{3/}	98.6	----	100.6		^{4/} 67.0
11----	104.7	91.5	111.2		^{4/} 83.9
12 ^{3/} ----	99.2	93.5	91.1		^{4/} 80.0
15----	^{5/} 98.6	----	101.0		^{5/} 98.9
28----	^{5/} 98.5	- -	94.9		^{5/} 92.9

^{1/} Recovery is based on morphine entering the step in question.

^{2/} Morphine in crude morphine liquor, condensate and evaporator rinses are included. Recovery is based on morphine in extract liquor.

^{3/} Ferricyanide method of analysis for morphine was used throughout for these tests.

^{4/} Recovery was low because of morphine lost in tars removed by filtration.

^{5/} Morphine recovered by extraction of tars is also included.

TABLE 20.--Analyses of crude morphine liquors

Sample No.	Recovery method	Physical state	Solids content	Ash content	Spec. grav. 30°/15° C.	pH	NU analysis		Mallinckrodt analyses		
							Morphine	Percent	Morphine	Co-deine	The-baine
			Percent	Percent				Percent	Percent	Percent	Percent
3701-	Ion	Liquid and									
130-49	exchange	some	18.0	10.1	1.117	---	2.16		1.62	0.248	0.086
		solids									
3701-	Distil-										
136-37	lation	do	22.2	----	1.104	5.0	3.64		2.28	.404	.219

TABLE 21.--Summary of estimated production costs
for poppy-processing plant^{1,2/}

Item	Ion exchange recovery method
	<u>Daily costs</u>
Raw materials and supplies other than crude	
poppy straw-----	\$701.39
Utilities-----	868.63
Labor and supervision-----	754.40
Prorated charges for milling straw prior to	
storage (first-break operations)-----	66.18
Maintenance-----	423.80
Fixed charges-----	<u>776.83</u>
Costs exclusive of crude poppy straw---	\$3,591.23
Crude poppy straw-----	36,366.67
Total production costs, per day-----	<u>39,957.90</u>
	<u>Cost/lb. anhydrous morphine^{3/}</u>
Production costs exclusive of crude poppy	
straw-----	\$16.18
Cost of crude poppy straw-----	163.82
Total production costs-----	180.00
Less credit for codeine present in crude	
morphine liquor at \$6.00 per ounce-----	
(37 lb. of codeine produced daily)-----	16.00

TABLE 21.--Continued

Item	Cost/lb. anhydrous morphine ^{3/}
Adjusted production costs -----	<u>\$164.00</u>
Adjusted production costs, per ounce of anhydrous morphine ^{3/} -----	10.25

^{1/} The plant daily produces crude morphine liquor containing 222 pounds of anhydrous morphine (quantity required to produce 200 pounds of refined morphine) and operates 24 hours per day, 300 days per year.

^{2/} 1958 basis.

^{3/} Exclusive of administrative and selling costs.

TABLE 22.--Summary of fixed cost of poppy-processing plant^{1,2/}

1. Land-----	:	\$40,000 :	:	:
2. Site preparation-----	:	<u>5,000 :</u>	:	:
	:	:	:	\$45,000
3. Buildings-----	:	731,000 :	:	:
4. Service facilities-----	:	230,000 :	:	:
5. Equipment for utilities,	:	:	:	:
including installation,	:	:	:	:
piping, wiring, and	:	:	:	:
instrumentation-----	:	434,000 :	:	:
6. Process equipment, includ-	:	:	:	:
ing installation, piping,	:	:	:	:
wiring, and	:	:	:	:
instrumentation-----	:	1,361,000 :	:	:
7. Total of items 3, 4, 5,	:	:	:	:
and 6-----	:	:	\$2,756,000 :	:
8. Engineering costs, 5% of	:	:	:	:
\$2,756,000-----	:	138,000 :	:	:
9. Contingency and con-	:	:	:	:
tractor's fees, 30% of	:	:	:	:
\$2,756,000-----	:	827,000 :	:	:
	:	:	:	:
	:	:	:	:

TABLE 22.--Continued

10. Total of items 8 and 9--	:	:	:
	:	:	:
11. Total cost of equipment	:	:	:
and buildings (sum of	:	:	:
items 7 and 10)-----	:	:	:
	:	:	:
12. Total fixed capital-----	:	:	:
	:	:	:
	:	:	:

1/ Ion-exchange recovery method; crude morphine liquor containing 222 pounds of anhydrous morphine produced daily from 36.366 tons of crude poppy straw.

2/ 1958 basis.

TABLE 23. Investment cost of land, buildings, and service facilities
(Ion-exchange recovery method)

Item	Description and quantity	Estimated cost
Land-----	40 acres	\$40,000
Site preparation-----		<u>5,000</u>
Cost of land and site preparation-----		45,000
Storage buildings-----	7 - Butler building, type RFG, 50 feet wide x 440 feet long x 14 feet side wall, aluminum and steel construction. Buildings erected, electric lights installed and floors paved with asphalt surfacing. Six buildings are for storage of partially ground straw and one for seed-bearing fraction	462,000
Straw-processing building	1 - 3-story building; first and second floors 50 feet wide x 80 feet long, third floor 20 feet wide x 80 feet long; open-type construction, 10-foot ceilings	72,000
Chemical-processing building-----	1 - 3-story building, each floor 50 feet wide x 100 feet long, 10-foot ceilings, open-type construction	122,000

TABLE 23.--Continued

Item	Description and quantity	Estimated cost ^{1/}
Administration and maintenance building-----	1 - Single-story building, 5,420 square feet floor space, to house offices, warehouse, mechanical shops, laboratory, locker room, and garage. Constructed of corrugated iron	\$38,000
Boiler house-----	1 - Single-story building, 44 feet wide x 60 feet long x 20 feet wall, corrugated iron construction. Building to house steam boiler and Dowtherm vaporizer.	<u>37,000</u> \$731,000
Cost of buildings-----		
Service facilities-----	Railroad siding, sewer, fence, fire protection, road, asphalt-paving for crude straw-unloading and temporary storage apron, and wind-break walls for crude straw apron, and for stem storage area	230,000
Total cost of land, buildings and service facilities		\$1,006,000

^{1/} 1958 basis.

TABLE 24.--Estimated investment cost of process equipment
(Ion-exchange recovery method)

		<u>Estimated cost</u> ^{1/}
Delivered cost of process equipment:		
<u>Group</u> ^{2/} <u>No.</u>	<u>Operation</u>	
1.	Handling and storage of chemicals, solvents, and product-----	\$29,500
2.	Preparation of straw for storage--	194,200
3.	Storage and handling of straw----	27,000
4.	Preparation of meal for extraction-----	51,500
5.	Extraction, pressing, and desol- ventizing of poppy meal-----	175,500
6.	Ion exchange-----	77,700
7.	Concentration of cation eluate by evaporation-----	70,100
8.	Solvent recovery-----	98,000
9.	Disposal of stems and desol- ventized solids-----	19,000
Delivered cost of equipment listed above--		742,500
Installation, 43% of delivered cost of equipment-----		319,300

TABLE 24.--Continued

	<u>Estimated cost</u> ^{1/}
Equipment installed -----	\$1,061,800
Piping and wiring, 36% of delivered cost of equipment -----	267,300
Process equipment, piping, and wiring installed -----	1,329,100
Instrumentation, 3% of installed cost of equipment -----	31,900
Total cost of process equipment, piping, wiring, and instrumentation installed -----	1,361,000

^{1/} 1958 basis.

^{2/} See Table 31 for detailed list of equipment.

TABLE 25.--Estimated investment cost of equipment for utilities
(Ion-exchange recovery method)

Equipment for utilities	Estimated cost ^{1/}
1. List of equipment and delivered cost:	
a. Dowtherm vaporizer, 2.5 mil. B.t.u./hour	
Dowtherm vaporizer auxiliaries - stack, draft fan, vent condenser, controls, 750-gallon steel auxil- iary fuel tank, and 10,000 pounds of Dowtherm A for initial charge---	\$25,000
b. Steam boiler, 37,500 pounds/hour at 75 p.s.i.g.-----	75,000
c. Raw water intake and filtering in- stallation, 2,500 g.p.m.-----	21,000
d. Main water supply pump, 2,500 g.p.m., at 150 feet-----	3,000
e. Cooling tower, 1,500 g.p.m., cooling from 85° to 76° F.-----	15,000
Cooling tower pump, 1,500 g.p.m. at 100 feet-----	1,900
f. Storage tank for process water, 5,000-gallon capacity, rubber- lined steel-----	2,800

TABLE 25.--Continued

Equipment for utilities	Estimated cost ^{1/}
g. Demineralized water system,	
50 g.p.m. capacity-----	\$24,400
Demineralized water surge tank,	
20,000-gallon capacity, rubber-	
lined steel-----	6,000
Demineralized water pump, 100 g.p.m.	
at 50 feet-----	460
h. Air compressors, 1-40 c.f.m. at	
100 p.s.i.g., 1-1,500 c.f.m. at	
40 p.s.i.g.-----	12,300
i. Electrical distribution system,	
700 kw. capacity-----	50,000
2. Delivered cost of equipment listed above--	236,900
3. Installation, 43% of delivered cost of	
equipment-----	101,900
4. Equipment installed-----	338,800
5. Piping and wiring, 36% of delivered cost	
of equipment-----	85,300
6. Equipment, piping, and wiring installed--	424,100

TABLE 25.--Continued

Equipment for utilities	Estimated cost ^{1/}
7. Instrumentation, 3% of installed cost of equipment-----	\$10,200
8. Installed cost of above equipment for utilities including piping, wiring, and instrumentation (sum of items 4, 5, and 6)-----	434,300

^{1/} 1958 basis.

TABLE 26.--Estimated cost of raw materials and supplies

(Ion-exchange recovery method)

Daily requirements	Daily ^{1/} cost	Cost/lb. anhydrous morphine
Isobutyl alcohol, technical grade, 2,000 pounds at \$0.135/lb.-----	\$270.00	\$1.22
Isopropyl alcohol, 91 volume %, tech- nical grade, 50 gallons at \$0.58/ gallon-----	29.00	0.13
Sulfuric acid, 66° Baumé, technical grade, 4,350 pounds at \$30/ton-----	65.25	.29
Sodium hydroxide, liquid, 50% commer- cial grade, 4,530 pounds at \$3.75/ cwt.; 100% basis-----	84.95	.38
Filter aid, diatomaceous earth, 204 pounds at \$75/ton-----	7.65	.03
Ion-exchange resins, replacement costs ^{2/} :		
Cation resin, 5.8 cubic feet at \$15/cubic foot-----	87.00	.39
Anion resin, 0.83 cubic feet at \$50/cubic foot-----	41.50	.19
Ammonia, anhydrous, commercial grade, 648 pounds at \$105/ton-----	34.02	.15

TABLE 26.--Continued

Daily requirements	Daily ^{1/} cost	Cost lb. anhydrous morphine
Limestone, lump, 4,000 pounds at		
\$10 ton-----	\$20.00	\$0.09
Equipment supplies, 0.5% of		
\$3,721,000 ³ -----	<u>62.02</u>	<u>.28</u>
Raw materials exclusive of crude		
poppy straw-----	701.39	3.15
Crude poppy straw, 36.367 tons at		
\$1,000 ton-----	\$36,366.67	\$163.81

^{1/} Costs of chemicals taken as of June 1959.

^{2/} Useful life of resins estimated at 200 cycles.

^{3/} Fixed plant investment for items that depreciate in value, exclusive of land and site improvement.

TABLE 27.--Estimated cost of utilities

(Ion-exchange recovery method)

Daily requirements	Daily costs	Cost/lb. anhydrous morphine
Steam 543,000 pounds at \$0.75/1,000 pounds--	\$407.25	\$1.83
Water:		
Filtered river water at 85° F.,		
3,168,000 gallons at \$0.075/1,000		
gallons-----	237.60	1.07
Water from cooling tower at 76° F.,		
2,016,000 gallons at additional cost		
of \$0.02/1,000 gallons-----	40.32	0.18
Demineralized water, 85° F., 32,400 gal-		
lons at \$0.35/1,000 gallons-----	11.34	.05
Electricity, 10,100 kw.-hour at \$0.01 kw.-		
hour-----	101.00	.45
Compressed air:		
49,000 cubic feet free air at 80 p.s.i.g.;		
at \$0.016/1,000 cubic feet-----	0.78)
241,600 cubic feet free air at 20 p.s.i.g.;)
oil-free, at \$0.020/1,000 cubic feet----	4.83) .03
14,400 cubic feet free air at 20 p.s.i.g.;)
oil- and water-free, at \$0.070/1,000)
cubic feet-----	1.01)
Heat from Dowtherm vaporizer, 51,600,000		
B.t.u. at \$1.25/1,000,000 B.t.u.-----	64.50	.29
Total-----	\$868.63	\$3.90

TABLE 28.--Estimated cost of maintenance and fixed charges
(Ion-exchange recovery method)

Maintenance	Daily costs	Cost/lb. anhydrous morphine
Buildings and land, 2%/year on \$987,000 ^{1/}	\$65.80	\$0.30
Service facilities, 5%/year on \$311,000 ^{2/}	51.83	.23
Process equipment, 5%/year on \$1,837,000 ^{3/}	306.17	1.38
Total-----	\$423.80	\$1.91
<u>Fixed charges</u>		
Taxes and insurance--not included		
Depreciation:		
Buildings, 5%/year on \$987,000 ^{1/}	\$164.50	\$0.74
Process equipment, 10%/year on		
\$1,837,000 ^{3/} -----	612.33	2.76
Total-----	\$776.83	\$3.50

^{1/} \$987,000 = \$45,000 for land + \$731,000 (1.00 + 0.05 + 0.30) for buildings.

^{2/} \$311,000 = \$230,000 (1.00 + 0.05 + 0.30) as cost of service facilities, including engineering costs, contingency, and contractor's fees.

^{3/} \$1,837,000 = \$1,361,000 (1.00 + 0.05 + 0.30) as cost of process equipment, including engineering costs, contingency, and contractor's fees. The cost of equipment such as steam boiler, water-cooling tower, etc., is not included since the charges for the various utilities include maintenance and fixed charges.

TABLE 29.--Estimated cost of labor and supervision

(Ion-exchange recovery method)

Classification	Men per shift	Shifts per day	Man- hours per day	Hourly wage rate	Daily cost
<u>Helpers</u> for transportation of first-break stems					
and seed-bearing fractions out of storage and					
clean seed back to storage-----	3	1	24	\$2.00	\$48.00
<u>Operator</u> for equipment for second, third, and					
fourth breaks and seed cleaner-----	1	3	24	2.50	60.00
<u>Operator</u> for extractor, Davenport press, desol- ventizer, and Vallez filters---	1	3	24	2.50	60.00
<u>Helper</u> for above operator	1	3	24	2.00	48.00
<u>Operators</u> for plate and frame filter presses, ion-exchange columns, eluate neutralization step-----	2	3	48	2.50	120.00
<u>Helper</u> for above operators-----	1	3	24	2.00	48.00
<u>Operator</u> for eluate evaporators, IPA wash evaporators, and carbon adsorption systems-----	1	3	24	2.50	60.00
<u>Helper</u> for above operator-----	1	3	24	2.00	48.00

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TABLE 29.--Continued

Classification	Men per shift	Shifts per day	Man- hours per day	Hourly wage rate	Daily cost
<u>Operator for 3 distillation columns</u> -----	1	3	24	\$2.50	\$60.00
<u>Storekeeper and warehouse man</u> -----	1	1	8	2.00	16.00
<u>Chemist</u>	1	1	8	3.50	28.00
<u>Laboratory technicians</u>	1	2	16	2.25	36.00
<u>Shift supervisors (chemical engineers or chemists)</u>	1	3	24	3.50	84.00
<u>Plant supervisor</u>	1	1	8	4.80	<u>38.40</u>
Total daily cost-----					\$754.40

TABLE 30.--Estimated cost of first-break operations

(Ion-exchange recovery method)

Classification	Men per shift	Shifts per day	Man- hours per day	Hourly wage rate	Daily cost
A. Labor and Supervision:					
Operator of tractor with pusher blade-----	2	3	48	\$2.00	\$96.00
Laborer for unloading trucks-----	2	3	48	2.00	96.00
Operator of motor-driven sweeper-----	1	3	24	2.00	48.00
Operator of first-break straw process- ing equipment-----	1	3	24	2.50	60.00
Laborer for putting partially ground straw in storage-----	4	3	96	2.00	192.00
Laborer for putting seed-bearing fraction in storage-----	2	3	48	2.00	96.00
Laborer for putting stems from first break in storage-----	2	3	48	2.00	96.00
Foreman-----	1	3	24	3.25	78.00
Plant superintendent-----	1	1	8	4.80	38.40
Total daily cost-----					\$800.40

Total cost of labor and supervision for 18 days is \$14,407.20

TABLE 30.--Continued

				Cost of opera- tion	Operating cost
<u>B. Miscellaneous Equipment:</u> ^{1/}					
	<u>Item and quantity</u>		<u>Basis</u>		
2	Rubber-tired tractors equipped with bulldozer blades-----		Government-owned	\$2/hour	\$1,728
1	Motor-driven sweeper-----		Leased	3 do.	1,296
1	1-1/2-ton truck-----		Government-owned	2 do.	<u>864</u>
	Total-----				\$3,888
<u>C. Electricity:</u>					
	Power required for equipment in Group No. 2-----		Hp.		
	Power required for equipment in Group No. 3-----		284.5		
	Power required for equipment in Group No. 9-----		95.0		
	Power required for equipment in Group No. 9-----		<u>100.5</u>		
	Total-----		480.0		

Kw.-hours required = 480 X 0.746 = 358

Cost = 358 kw.-hours X 24 hours/day X 18 days/season X \$0.01/kw.-hours = \$1,546.56

TABLE 30.--Continued

Classification	Men per shift	Shifts per day	Man- hours per day	Hourly wage rate	Daily cost
D. Air:					
Volume of air required for 5 air-controlled roller mills is 30 c.f.m.					
Cost = 30 cubic feet/minute X 60 minutes/ hour X 24 hours/day X 18 days/year X \$0.016/1,000 cubic feet = \$12.44					
<u>Summary of Costs:</u>					
Labor and supervision-----				\$14,407.20	
Miscellaneous equipment-----				3,888.00	
Electricity-----				1,546.56	
Air-----				<u>12.44</u>	
Total-----				\$19,854.20	
Costs for first-break processing operations prorated over 300 days' operation for poppy-processing plant = \$19,854.20 ÷ 300 = \$66.18.					
Costs for first-break operations prorated per pound of anhydrous morphine = \$0.29.					

✓ Operating cost is based upon equipment being operated 24 hours/day for 18 days during the time the crude poppy straw is received, processed through the first-break, and placed in storage.

TABLE 31.--List of process equipment and estimate of cost
(Ion-exchange recovery method)

Item ^{1/}	Estimated delivered cost ^{2/}
Group No. 1 - Handling and storage of chemicals, solvents, and product	
7 - Storage tanks, steel:	
1 99+% IBA, 12,000 gallons	
1 Anhydrous NH ₃ , 6,000 gallons	
1 66° Baumé H ₂ SO ₄ , 12,000 gallons	
1 50% NaOH, 12,000 gallons	
1 Fuel oil, 35,000 gallons	
2 Crude morphine liquor, 10,000 gallons	
6 - Centrifugal pumps, steel:	
1 99+% IBA, 15 g.p.m. at 40 foot head	
1 91% IPA, 5 g.p.m. at 20 foot head	
1 66° Baumé H ₂ SO ₄ , 7 g.p.m. at 30 foot head:	
1 50% NaOH, 12 g.p.m. at 40 foot head	
1 Fuel oil, 50 g.p.m. at 40 foot head	
1 Crude morphine liquor from storage to tank car, 100 g.p.m. at 50 foot head	
Total horsepower for Group No. 1 = 8.00	
Total cost of equipment for Group No. 1-----	\$29,500

TABLE 31.--Continued

Item ^{1/}	: Estimated : delivered : cost ^{2/}
10 Tramp-iron separators, magnetic	:
10 Cut hay feeders, B. F. Gump Co. type No. 116B, steel	:
5 Roller mills, double type, LePage rolls, 10 X 42 inches	:
10 Double screen scalpors	:
1 Fan, with two 51-inch dust collectors	:
Total horsepower for Group No. 2 = 284.50	:
Total cost of equipment for Group No. 2-----	: \$194,200
Group No. 3 - Handling of straw into and out of storage	:
3 Storage bins, steel:	:
1 Surge bin, 300 cubic feet, hopper bottom, for partially ground straw	:
1 Day's run bin, 8,300 cubic feet, hopper bottom, for partially ground straw	:
1 Day's run bin, 1,340 cubic feet, conical bottom, for seed-bearing fraction	:
2 Rotary valves, steel, 5 inch diameter	:

TABLE 31.--Continued

Item ^{1/}	Estimated delivered cost ^{2/}
1 Blower, 700 c.f.m. free air at 10 p.s.i.g.	:
1 Steel tubing for pneumatic conveying system, 4-1/2 inch O.D., 660 feet	:
6 Valves, 4-1/2 inches	:
1 Rubber or flexible metallic hose for pneumatic conveying system, 4-1/2 inch O.D., 400 feet	:
1 Cyclone, 700 cubic feet free air/minutes	:
1 Screw conveyor, steel, 12-inch diameter, 25 feet long, 745 cubic feet/hour of seed-bearing fraction	:
1 Spaced bucket elevator, 35 feet long, 745 cubic feet/hour of seed-bearing fraction	:
1 Hopper, steel, 150 cubic feet	:
1 Truck, 1-1/2 ton, with 364 cubic foot box and hydraulic or mechanical lift	:
1 Portable elevator, steel, 9-inch diameter screw, 60 feet long, maximum elevation 40 feet, 3,750 cubic feet/hour of seed- bearing fraction	:
Total horsepower for Group No. 3 = 95.00	:
Total cost of equipment for Goupr No. 3-----	\$27,000

TABLE 31.--Continued

Item ^{1/}	: Estimated : delivered : cost ^{2/}
Group No. 4 - Preparation of meal for extraction	:
5 Screw conveyors, steel:	:
1 9-inch diameter, 25 feet long, 293 cubic feet/hour of partially ground straw	:
1 9-inch diameter, 15 feet long, 208 cubic feet/hour to second break	:
1 6-inch diameter, 50 feet long, 167 cubic feet/hour of meal	:
1 6-inch diameter, 10 feet long, 45 cubic feet/hour of seed-bearing fraction	:
1 6-inch diameter, 70 feet long, 167 cubic feet/hour of meal	:
5 Spaced bucket elevators:	:
1 20 feet long, 293 cubic feet/hour of par- tially ground straw	:
1 20 feet long, 176 cubic feet/hour to third break	:
1 20 feet long, 77 cubic feet/hour to fourth break	:
1 18 feet long, 45 cubic feet/hour of seed fraction	:
1 40 feet long, 167 cubic feet/hour of seed fraction	:

TABLE 31.--Continued

Item ^{1/}	Estimated delivered cost ^{2/}
2 Storage bins: One wood, 208 cubic feet of seed; one steel, 5,000 cubic feet of meal	
2 Double screen scalpers	
1 Seed cleaner	
1 Dust collector	
3 Tramp-iron separators, magnetic	
1 Exhaust fan, with two 39-inch dust collectors	
2 Roller mills, double type, corrugated 10 X 42-inch rolls, for second, third, and fourth breaks	
2 Low head, gyratory sifters with 55 square feet of bolting area	
Total horsepower for Group No. 4 = 51.25	
Total cost of equipment for Group No. 4-----	\$51,500
Group No. 5 - Extraction, pressing, and desolventizing of poppy meal	
2 Screw conveyors, steel:	
1 6-inch diameter, 18 feet long, 200 cubic feet/hour of meal	
1 6-inch diameter, 10 feet long, 200 cubic feet/hour of meal	

TABLE 31.--Continued

Item ^{1/}	Estimated delivered cost ^{2/}
1 Mixing conveyor, steel, 20-inch diameter, 20 feet long, combination ribbon, paddle type, 233 cubic feet/hour	:
1 Paddle-type conveyor, steel, 20-inch diameter, four 40-foot sections and one 20-foot section, 233 cubic feet/hour	:
2 Spaced-bucket elevator, one 30 feet long, 200 cubic feet/hour of meal; one 40 feet long, 200 cubic feet/hour of meal	:
1 Gravimetric feeder, 3 cubic feet/minute capacity	:
1 Flow mixer, for dissolving NH ₃ gas in wetting liquor, steel	:
1 Kennedy-type extractor, iron and steel, 20 stages, capacity 8.8 cubic feet wetted meal per stage, vapor-tight construction	:
1 Surge tank No. 1 for extract liquor, steel, 2,000 gallons, with top entering agitator	:
4 Steel tanks:	:
1 83% IBA makeup, 400 gallons	:
1 Solvent A feed, 3,000 gallons	:

TABLE 31.--Continued

Item ^{1/}	: Estimated : delivered : cost ^{2/}
1 Solvent B feed, 1,500 gallons	:
1 Surge No. 2 for extract liquor, 2,000 gallons	:
1 Propeller-type mixer for 83% IBA makeup tank	:
5 Centrifugal pumps, steel:	:
1 83% IBA, 10 g.p.m. at 30 foot head	:
1 Solvent A feed, 22 g.p.m. at 30 feet head	:
1 Solvent B feed, 11.6 g.p.m. at 30 feet head	:
1 Surge tank No. 1, 25.4 g.p.m. at 120 feet head	:
1 Wetting liquor, 8.5 g.p.m. at 30 feet head	:
2 Preheaters, steel, tube and shell:	:
1 Solvent A, 20.9 square feet	:
1 Solvent B, 4.4 square feet	:
2 Enclosed, rotating leaf filters, 13 leaves, 97 square feet, 12 cubic feet cake capacity, cast iron and steel	:
1 Continuous dewatering press, with vapor-tight housing	:

TABLE 31.--Continued

Item ^{1/}	Estimated delivered cost ^{2/}
1 Desolventizer condenser, tube and shell, 125 square feet, steel	:
1 Desolventizer condensate subcooler, shell and tube, 35 square feet, steel	:
1 Desolventizer decanter, steel, 400 gallons	:
Total horsepower for Group No. 5 = 108.75	:
Total cost of equipment for Group No. 5-----	: \$175,500
Group No. 6 - Ion Exchange	:
16 Tanks:	:
2 Extract surge, each 2,000 gallons, steel	:
1 Precoat mixing, 100 gallons, steel	:
2 5% H ₂ SO ₄ feed, each 2,500 gallons, rubber-lined steel	:
2 4% NaOH feed, each 2,500 gallons, steel	:
1 IPA feed, 1,500 gallons, steel	:
1 Spent IPA, 1,500 gallons, steel	:
2 50% H ₂ SO ₄ feed, each 100 gallons, rubber- lined steel	:
2 Eluate neutralization, each 4,000 gallons, steel	:

TABLE 31.--Continued

Item ^{1/}	: Estimated : delivered : cost ^{2/}
2 1% NaOH feed, each 400 gallons, steel	:
1 Anion regenerant, 2,500 gallons, steel	:
14 Agitators for tanks, top-entering	:
8 Centrifugal pumps:	:
1 Surge tank No. 2, 16.9 g.p.m. at 70 foot head, steel	:
1 Surge tank No. 3, 50 g.p.m. at 160 foot head, steel	:
1 Precoat slurry, 31.7 g.p.m. at 30 feet head, steel	:
1 Surge tank No. 4, 16.9 g.p.m. at 35 foot head, steel	:
1 5% H ₂ SO ₄ , 4% NaOH, and IPA, 175 g.p.m. at 30 foot head, Worthite	:
1 Neutralized cation eluate, 25.6 g.p.m. at 10 foot head, steel	:
1 1% NaOH feed, 50 g.p.m. at 20 foot head, steel	:
1 Spent anion regenerant, 4.8 g.p.m. at 20 foot head, steel	:
1 Cooler for extract liquor, shell and tube, 150 square feet, steel	:

TABLE 31.--Continued

Item ^{1/}	Estimated delivered cost ^{2/}
1 Vertical, long-tube evaporator, 429 square feet, 304 stainless-steel tubes, steel body	
1 Agitated, falling-film-type evaporator, 66 square feet, 304 stainless steel	
3 Condensers, shell and tube, steel:	
1 2,100 square feet	
1 338 square feet	
1 3.5 square feet	
3 Condensate and product receivers, steel, each 200 gallons	
4 Centrifugal pumps:	
1 Condensate, 20.7 g.p.m. at 35 foot head, steel	
1 Evaporator feed, 4.5 g.p.m. at 20 foot head, steel	
1 Condensate, 3.5 g.p.m. at 35 foot head, steel	
1 Product, 1.3 g.p.m. at 55 foot head, steel	
2 Carbon adsorbers, each 4 feet diameter X 4 feet steel tank with 300 pounds activated carbon	

TABLE 31.--Continued

Item ^{1/}	: Estimated : delivered : cost ^{2/}
1 Blower, 1,500 cubic feet free air/minute at 12 inches water static pressure	:
1 Steam ejector, 2-stage with intercondenser	:
Total horsepower for Group No. 7 = 21.25	:
Total cost of equipment for Group No. 7-----	\$70,100
Group No. 8 - Solvent recovery	:
2 Feed tanks, steel, one 2,500 gallons, one 1,000 gallons	:
2 Agitators for tanks, top-entering	:
7 Centrifugal pumps:	:
1 Column No. 1 feed, 21.3 g.p.m. at 10 foot head, steel	:
1 Column No. 1 bottoms, 19.3 g.p.m. at 20 foot head, steel	:
1 Spent IPA feed, 3.6 g.p.m. at 5 foot head, steel	:
1 Column No. 2 feed, 3.1 g.p.m. at 25 foot head, steel	:
1 Column No. 2 bottoms, 6.1 g.p.m. at 25 foot head, steel	:
1 Column No. 3 feed, 6.8 g.p.m. at 35 foot head, steel	:

TABLE 31.--Continued

Item ^{1/}	: Estimated : delivered : cost ^{2/}
:	
:	
1 Column No. 3 bottoms, 6.1 g.p.m. at	
25 feet head, steel	
:	
1 Distillation column No. 1, 2-3/4 feet	
diameter, 30 bubble-cap trays, 18-inch	
spacing, steel	
:	
1 Distillation column No. 2, 4.0 feet diameter,	
50 bubble-cap trays, 18-inch spacing, steel:	
:	
1 Distillation column No. 3, 17-inch I.D., steel	
column with 25 feet of 1-1/2 inch ceramic	
Raschig ring packing	
:	
8 Condensers and coolers, shell and tube, steel:	
:	
1 100 square feet	
:	
1 24 square feet	
:	
1 112 square feet	
:	
1 494 square feet	
:	
1 26 square feet	
:	
1 347 square feet	
:	
1 16 square feet	
:	
1 10 square feet	
:	
1 Condensate receiver, 400 gallons, steel	
:	
3 Reboilers, shell and tube, kettle-type, steel:	
:	

TABLE 31.--Continued

Item ^{1/}	: Estimated : delivered : cost ^{2/}
1 73 square feet	:
1 350 square feet	:
1 18 square feet	:
1 Vertical, long-tube evaporator, 59 square feet, all steel	:
2 Jacketed kettles, each 200 gal., 200 square feet, heating surface, with anchor-type agitator, steel	:
1 Decanter, 500 gallons, steel	:
2 Carbon adsorbers, each: Horizontal steel tank 8-foot diameter X 16 feet, with 11,420 pounds activated carbon	:
2 Blowers, steel:	:
1 2,500 cubic feet free/minute at 12 inches	:
1 500 cubic feet free/minute at 12 inch water static pressure	:
Total horsepower for Group No. 8 = 19.00	:
Total cost of equipment for Group No. 8-----	\$98,000

TABLE 31.--Continued

Item ^{1/}	Estimated delivered cost ^{2/}
Group No. 9 - Disposal of stems and desolventized meal	
1 Stem chopper, capacity 2,685 cubic feet of stems/hour	
2 Cyclone collectors, each: 575 cubic feet free air/minute	
2 Rotary values, steel, 5 inches diameter	
1 Blower, 575 cubic feet free air/minute at 10 p.s.i.g. delivery pressure	
1 Steel tubing for pneumatic system, 600 feet, 4 inch O.D.	
1 Rubber hose for pneumatic system, 400 feet, 4 inch O.D.	
2 Day's run storage bins, steel:	
1 5,000 cubic feet	
1 6,000 cubic feet	
4 Screw conveyors, steel:	
1 6-inch diameter, 50 feet long, 44 cubic feet/hour	
1 6-inch diameter, 30 feet long, 44 cubic feet/hour	

TABLE 31.--Continued

Item ^{1/}	: Estimated : delivered : cost ^{2/}
1 6-inch diameter, 90 feet long, 44 cubic feet/hour	: : :
1 6-inch diameter, 80 feet long, 156 cubic feet/hour	: : :
Total horsepower for Group No. 9 = 109.5	: :
Total cost of equipment for Group No. 9-----	: \$19,000 :
Total cost of equipment for Group Nos. 1-9-----	: \$742,500 : :

^{1/} Driven units include motor and drive.

^{2/} 1958 basis.

^{3/} Laboratory tests indicated that a sample of Koroseal-covered steel and a sample of Uscolite, the latter, to be used for process lines to the ion-exchange equipment, will not swell or soften when exposed to the extract liquor at room temperature.

TABLE 32.--Morphine recovery in various
process steps

Process step	Recovery of morphine	
	Design	Experimental
	Percent	Percent
Extraction of morphine from meal---	95.0	96.9
Filtration of extract liquor-----	100.0	100.0
Adsorption of morphine on cation		
exchanger-----	98.0	98.8
Elution of morphine from cation		
exchanger and neutralization		
of eluate-----	95.5	96.7
Concentration of eluate by		
evaporation-----	^{1/} 96.7	94.6
Overall recovery of morphine from		
poppy meal to crude morphine		
liquor-----	86.0	90.6

^{1/} Assuming that at least one-half of the morphine present in tars encountered in the experimental work can be recovered by procedures now used by commercial refiners of opium to handle similar materials.

TABLE 33.--Quantity of morphine required in various process streams

Refined morphine required (Mallinckrodt analysis)-----	60,000 pounds/year \div 300 days/year = 200 pounds/day	
Morphine in crude morphine liquor delivered to manufacturing chemists (Mallinckrodt analysis)-----	$200/0.90^{1/}$ = 222 pounds/day	
Morphine in crude morphine liquor-----	$2.15^{2/}$ X 222 = 296 pounds/day or 12.33 pounds/hour	
Morphine in feed to evaporator-----	1.62	
Morphine adsorbed on new cation exchanger---	12.33/0.967 = 12.75 pounds/hour	
Morphine content of spent IPA wash when cation exchanger is new:	12.75/0.955 = 13.35 pounds/hour	
a. Volume of cation exchanger = 128.84 cubic feet/column		
b. Length of cycle = 10 hours		
c. Number of IPA washes per 10-hour cycle = 3, i.e., 1 wash every 3-1/3 hours		

TABLE 33.--Continued

Additional quantity of morphine that must	:	
be adsorbed when exchanger is near end	:	
of useful life-----	:	0.695 - 0.417 = 0.278 pounds/hour
Morphine adsorbed on used exchanger-----	:	13.35 + 0.28 = 13.63 pounds/hour
Morphine in cation influent-----	:	13.63/0.98 = 13.91 pounds/hour
Morphine in extract liquor-----	:	13.91/1.00 = 13.91 pounds/hour
Morphine in poppy meal entering extractor---	:	13.91/0.95 = 14.64 pounds/hour
Quantity of poppy meal to be extracted-----	:	14.64/0.007 = 2,090 pounds/hour
Quantity of crude straw to be processed in	:	
first break (24 hours/day for 18 days/	:	
year)-----	:	$\frac{2,090}{0.69} \times \frac{300}{18} = 50,508$ pounds/hour
	:	or
	:	50,508 X 24 X 18 = 21,819,000 pounds/year or
	:	10,910 tons/year

1/ Manufacturing chemists presumably can convert 90 percent or more of morphine in crude liquor into refined morphine.

2/ This correction factor is used since a sample of the crude liquor containing 2.16 percent morphine as analyzed at the Northern Division by the Matchett and Levine method was reported by the Mallinckrodt Chemical Works to have a morphine content of 1.62 percent.

TABLE 34.--Material balance over the first break
(18 days per year, 24 hours per day)

Basis: 1 hour

Process stream	Quantity
	<u>Pounds</u>
<u>Material in:</u>	
Crude poppy straw-----	50,508
<u>Material out:</u>	
Partially ground straw----	32,739
Seed-bearing fraction-----	9,617
First-break stems-----	8,056
Dust loss-----	<u>96</u>
Total-----	50,508

TABLE 35.--Material balance over second, third, and fourth
breaks and seed-cleaning operation
(300 days per year, 24 hours per day)

Process stream	Quantity
<u>Material in:</u>	<u>Pounds</u>
Partially ground straw-----	1,964
Seed-bearing fraction-----	<u>577</u>
Total-----	2,541
<u>Material out:</u>	
Poppy meal-----	2,090
Clean seed-----	197
Stems-----	177
Dust loss-----	<u>77</u>
Total-----	2,541

TABLE 36.--Material balance over extractor and Vallez filters

(300 days per year, 24 hours per day)

Basis: 1 hour

Process stream	Analyses ^{1/}	Ratio pound ^{2/} 100/pounds poppy meal ^{1/}	"M"	IBA	Water	Solids	Quantity
			Pounds	Pounds	Pounds	Pounds	Pounds
<u>Material in:</u>							
Poppy meal-----	9.7% moisture	100	14.63	-----	203	1,888	2,090
	90.3% solids						
	0.70% "M"						
Wetting liquor ^{2/} ----	91.45% IBA	166.7	7.02	3,186	228	72	3,484
	6.55% water						
	2.06% solubles						
	0.202% "M"						
Solvent A-----	83.55% IBA	440	0.15	7,683	1,499	14	9,196
	16.3% water						
	0.154% solubles						
	.0016% "M"						

TABLE 36.--Continued

Process stream	Analyses ^{1/}	Ratio pound/100/pounds poppy/ meal	"M"	IBA	Water	Solids	Quantity
			Pounds	Pounds	Pounds	Pounds	Pounds
Solvent B-----	84.0% IBA	231	0.44	4,061	740	33	4,834
	15.3% water						
	0.682% solubles						
	.0046% "M"						
Ammonia water-----	25.4% NH ₃	5	---	---	78	--	105
	74.6% water						
Total-----			22.24	14,930	2,748	2,007	19,709
Material out:							
Filtered extract							
Liquor ^{2.3/} -----	91.45% IBA	469.9	20.93	9,497	680	214	10,388
	6.55% water						
	2.06% solubles						
	0.202% "M"						

TABLE 36.--Continued

Process stream	Analyses ^{1/}	Ratio pounds/100/pounds poppy meal ^{1/}	"M"	IBA	Water	Solids	Quantity
			Pounds	Pounds	Pounds	Pounds	Pounds
"Fines" filter	73.0% M. and V.M.	5.2	0.16	72	7	29	108
cake ^{4/} -----	27.0% solids						
	66.8% IBA						
	6.2% water						
Solvent loss ^{5/} ---	67% IBA	0.34	---	5	2	--	7
	33% water						
Extracted meal ^{6/} --	80.8% M. and V. M.	441.0	70.83	5,395	2,056	1,770	9,221
	19.2% solids						
	58.5% IBA						
	22.3% water						
Total-----			21.92	14,967	2,745	2,013	19,724

^{1/} Average values from tests 24, 25, 26, and 28 except as explained in other footnotes.

^{2/} Composition assumed to be same as that of cation feed liquor.

^{3/} Total quantity of filtered extract liquor was calculated as the difference between "Material in" and the sum of the other three streams under "Material out"; then individual components were calculated based upon this quantity and the analysis as given.

TABLE 36. --Continued

Footnotes continued

4/ It was assumed that the "fines" filter cake will be subjected to a pressure of 35 p.s.i.g. in the rotary filter and that M. and V.M. will be reduced to 73 percent. Also assumed that the entrained liquor will have the same composition as the extract liquor.

5/ Assumed to be about 7 pounds of solvent per ton of poppy meal.

6/ Initial calculations based upon the extracted meal containing 79.5 percent M. and V.M. and entrained liquor having the same composition as solvent B showed a large deviation in the water balance and moderate deviations in the balance for IBA and solids. An adjustment was made by assuming that quantity of water in the extracted meal was equal to the difference between water in the incoming streams and the water in the other 3 outgoing streams. A similar adjustment was made for the solids. Finally, the quantity of IBA was assumed equal to 9,221 - (2,056 + 1,770). The composition as given for the extracted meal was calculated from these adjusted weights.

7/ Assumed equal to 5 percent of the "M" in the poppy meal plus two-thirds of that in the solvent A stream.

8/ Set equal to the total of "Material in" with some minor adjustments made later.

TABLE 37.--Continued

Process stream	Analyses	Ratio pound/100/pounds: poppy meal	IBA	Water	Solids	Quantity
			Pounds	Pounds	Pounds	Pounds
Press liquor--	84.0% IBA	231.2	4,061	740	33	4,834
	15.3% water					
	0.682% solubles					
Solvent loss ^{2/}	67% IBA	0.35	5	2	----	7
	33% water					
Total--			5,393 ^{6/}	2,061 ^{6/}	1,768 ^{6/}	9,221 ^{6/}

^{1/} Composition was calculated from weights of individual components as determined according to footnotes 3, 4, and 5.

^{2/} Assumed to be about 7 pounds of solvent per ton of poppy meal. Azeotropic composition assumed for solvent lost as vapors.

^{3/} Quantity of IBA was assumed equal to 4,380 - (1,319 + 1,735).

^{4/} Each of the components, water and solids, was calculated as the difference between the total and the sum of the quantities in the other two outgoing streams.

^{5/} Calculated as the difference between "Material in" and the weight of the other outgoing streams.

^{6/} Set equal to the total of "Material in" with some minor adjustments made later.

TABLE 37.--Material balance over dewatering press

(300 days per year, 24 hours per day)

Basis: 1 hour

Process stream	Analyses	Ratio pound /100/pounds: poppy meal	IBA	Water	Solids	Quantity
			Pounds	Pounds	Pounds	Pounds
<u>Material in:</u>						
Extracted meal---	80.8% M. and V.M.	441	5,394	2,056	1,770	9,221
	19.2% solids					
	58.5% IBA					
	22.3% water					
<u>Material out:</u>						
Pressed meal ^{1/} ---	60.4% M. and V.M.	209.5	1,327	1,319	1,735	4,380
	39.6% solids					
	30.3% IBA					
	30.1% water					

TABLE 38.--Material balance over flash desolventizer

(300 days per year, 24 hours per day)

Basis: 1 hour

Process stream	Analyses	Ratio pound/100/pounds poppy meal	IBA	IPA ^{1/}	Water	Solids	Quantity
			<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>
<u>Material in:</u>							
Pressed meal-----	39.6% solids	209.5	1,327	--	1,319	1,735	4,380
	30.3% IBA						
	30.1% H ₂ O						
Filter cake-----	73.0% M. and V.M.	5.2	72	--	7	29	108
	66.8% IBA						
	27.0% solids						
	6.2% water						
Total-----			1,399	--	1,326	1,764	4,488
<u>Material out:</u>							
Desolventized meal--	9.1% H ₂ O	93.2	-----	--	177	1,772	1,949
	90.9% solids						

TABLE 38.--Continued

Process stream	Analyses	Ratio pound/100 pounds poppy meal	IBA	IPA ^{1/}	Water	Solids	Quantity
			<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>
Condensate, at 30° C. ^{2/}	46.7% H ₂ O 53.3% IBA	(120.8)	(1,346)		(1,180)	----	(2,526)
Alcohol layer -----	78% IBA 4% IPA 18% H ₂ O	73.8	1,203	62	278	----	1,543
Water layer -----	78% IBA 1.8% IPA 91.2% H ₂ O	93.2	69	18	897	----	983
Total -----			1,272	80	1,352	1,772	4,475

^{1/} Consideration given to IPA only in determining composition of the two layers from the desolventizer condensate.

^{2/} Since the decanted alcohol layer from the bottoms of distillation column No. 2 will contain 5.2 percent IPA, 75.9 percent IBA, and 18.9 percent H₂O, the condensate from the flash desolventizer is assumed to contain these two alcohols in the same ratio. The condensate then would contain

TABLE 38.--Continued

Footnotes continued

[5.2/(5.2 + 75.9)] 53.3 or 3.4 percent IPA, 49.9 percent IBA, and 46.7 percent H₂O. At 30° C., this mixture should, according to a ternary solubility diagram prepared from laboratory data, divide into two layers--a water layer equal to 38.9 percent of the condensate, and an alcohol layer equal to 61.1 percent. The compositions of these two layers are given above.

TABLE 39.--Material balance over ion-exchange columns and
neutralization of cation eluate
(300 days per year, and 24 hours per day)

Basis: 1 hour

Process stream	Analyses	"M"	IBA	IPA	Water	Total solids	Quantity
		Pounds	Pounds	Pounds	Pounds	Pounds	Pounds
Material in:							
Cation columns							
Cation feed liquor	91.4% IBA	13.91	6,310	-----	452	142	6,904
	6.55% H ₂ O						
	2.06% Solids						
	0.20% "M"						
IPA wash	87.3% IPA	-----	-----	1,239	180	---	1,419
	12.7% H ₂ O						
4% NaOH solution						✓ 429	3,022
Water to rinse					2,901		
walls and resin	Tap water	-----	-----	-----	9,544	---	9,544
5% H ₂ SO ₄ solution		-----	-----	-----	2,841	---	2,991

TABLE 39--Continued

Process stream	Analyses	"M"	IBA	IPA	Water	Total solids	Quantity
		Pounds	Pounds	Pounds	Pounds	Pounds	Pounds
Water to rinse	Demineralized						
walls and resin---	water				8,533	---	8,533
50% H ₂ SO ₄ solution							
for neutraliza-							
tion of eluate----					75	---	149
1% NaOH solution----					453	16	458
Water to backwash							
resin, rinse	Demineralized						
walls, and resin--	water				3,601	---	3,601
Total-----		13.91	6,310	1,239	28,580	587	36,621
<u>Material out:</u>							
<u>Cation columns</u>							
Water displaced in							
"sweetening on"----	0.3% IBA		8		2,901	---	2,909

TABLE 39.--Continued

Process stream	Analyses	"M"	IBA	IPA	Water	Total solids	Quantity
		Pounds	Pounds	Pounds	Pounds	Pounds	Pounds
Spent IPA wash-----	0.90% Solids	0.70	495	709	306	14	1,524
	46.5% IPA						
	32.5% IBA						
	20.1% H ₂ O						
	0.046% "M"						
Water rinse of	1.32% Solids	12.75	378	540	11,629	168	12,715
walls, and neu-	4.25% IPA						
tralized cation	2.97% IBA						
eluate-----	0.100% "M"						
Water rinse of							
walls, and spent							
regeneration							
solution-----	.00015% "M"	0.01	-----	-----	8,428	1/ 104	8,532

TABLE 39.--Continued

Process stream	Analyses	"M"	IBA	IPA	Water	Total solids	Quantity
		Pounds	Pounds	Pounds	Pounds	Pounds	Pounds
<u>Anion columns</u>							
Water displaced in							
"sweetening on"---	0.3% IBA	-----	1	-----	454	---	455
Anion effluent-----	.94% Solids	0.17	5,291	-----	1,039	60	4/ 6,390
	82.8% IBA						
	16.24% H ₂ O						
	0.0026% "M"						
Backwash effluent,							
and spent anion							
regenerant							
solution-----	.00023% "M"	.02	5/ 137	-----	3,424	(1)	3,561
Total-----		13.65	6,310	1,249	28,181	346	36,086

1/ Calculated by difference for components in cation eluate.

2/ [Na⁺] ion content is expressed as Na₂SO₄.

3/ Calculated by assuming that IBA not accounted for in other streams must be in anion effluent.

TABLE 39.--Continued

Footnotes continued

4/ Quantity of anion effluent was then calculated on the basis of an IBA content of 82.8 percent.

5/ Calculated by assuming that 18.0 pounds of anion effluent are held up per cubic feet of anion resin. Remainder of spent regenerant solution was assumed to be water.

TABLE 40.--Material balance over vertical, long-tube evaporator and agitated, falling-film evaporator handling cation eluate

(300 days per year, and 24 hours per day)

Basis: 1 hour

Process stream	Analyses	"M"	IBA	IPA	HOH	Total solids	Quantity
		Pounds	Pounds	Pounds	Pounds	Pounds	Pounds
<u>Material in:</u>							
Neutralized cation	1.32% total solids						
eluate-----	4.25% IPA						
	2.97% IBA	12.75	378	540	11,629	168	12,715
	0.100% "M"						
	Water by difference						
Total-----		12.75	378	540	11,629	168	12,715
<u>Material out</u> ^{1/}							
Vertical, long-tube, evaporator	5.31% IPA						
	3.71% IBA ^{2/}						
condensate-----	90.98% water	-----	378	540	9,254	---	10,172

TABLE 40.--Continued

Process stream	Analyses	"M"	IBA	IPA	HOH	Total solids	Quantity
		Pounds	Pounds	Pounds	Pounds	Pounds	Pounds
Agitated, falling-film evaporator							
condensate-----	100% water ^{3/}	-----	---	---	1,772	---	1,772
Crude morphine liquor	21.8% total solids ^{4/}	^{5/} 12.33	---	---	^{6/} 603	^{7/} 168	771
Total-----		12.33	378	540	11,629	168	12,715

^{1/} Solvent loss not included.

^{2/} Analysis calculated by assuming fivefold concentration and that all of the alcohol present in the feed goes into this condensate.

^{3/} Assumed.

^{4/} Calculated as 168/771 or 21.8 percent.

^{5/} A 96.7-percent recovery of "M" for both evaporation steps was assumed.

^{6/} Calculated by difference.

^{7/} No solids were assumed lost during both evaporation steps.

TABLE 41.--Material balance over vertical, long-tube evaporator and jacketed kettles
for evaporation of the spent IPA wash
(300 days per year, and 24 hours per day)

Basis: 1 hour

Process stream	Analyses	IBA	IPA	HOH	Solids	Quantity
		Pounds	Pounds	Pounds	Pounds	Pounds
<u>Material in:</u>						
Spent IPA wash-----	0.90% solids	495	709	306	14	1,524
	46.5% IPA					
	32.5% IBA					
	20.1% water					
<u>Material out:</u>						
Combined overhead vapors ^{1/} ---	46.9% IPA	495	709	306	--	1,510
	32.8% IBA					
	20.3% water					
Tars-----		---	---	---	14	14
Total-----		495	709	306	14	1,524

^{1/} Quantity is the difference between "material in" and tars. Composition is calculated.

TABLE 42.--Material balance over distillation column No. 1

(300 days per year, and 24 hours per day)

Basis: 1 hour

Process stream	Analyses	IBA	IPA	H ₂ O	Quantity
<u>Material in</u> ^{1/} :					
Condensate from vertical,	5.31% IPA				
long-tube evaporator	3.71% IBA				
handling cation eluate-----	90.98% water				
Lower layer from decanter	2.4% IPA ^{4/}				
for distillation column	6.8% IBA				
No. 2-----	90.8% water				
Total-----		20	7	263	290
<u>Material out</u> :					
Distillate ^{2/} -----	44.3% IPA				
	32.1% IBA				
	23.6% water				
		398	547	9,517	10,462
		395	544	290	1,299

TABLE 42.--Continued

Process stream	Analyses	IBA	IPA	HOH	Quantity
		:Pounds	:Pounds	:Pounds	:Pounds
Bottoms ^{2/}	0.0328% IPA	2	3	9,228	9,233
	.0238% IBA				
	Balance is water				
Total		397	547	9,518	10,462

1/ Condensates from condensers for the two carbon adsorption systems will be fed also to distillation column No. 1. However, they were not included in this material balance.

2/ The composition and quantity of overhead was calculated assuming that both IPA and IBA distill over simultaneously at compositions approaching those of their respective azeotropes with water.

3/ The quantity of bottoms was assumed to be the difference between feed and overhead. The total alcohol content of the bottoms was set at 0.0156 mole percent and the ratio of the two alcohols was assumed to be the same as that in the feed.

4/ Composition of lower layer taken from ternary solubility diagram for IPA-IBA-H₂O system. See Figure 15.

TABLE 43.--Material balance over distillation column No. 2
(300 days per year, and 24 hours per day)

Basis: 1 hour

Process stream	Analyses	IBA	IPA	HOH	Quantity
		Pounds	Pounds	Pounds	Pounds
<u>Material in:</u>					
Condensate from distillation	44.3% IPA				
column No. 1	32.1% IBA	395	544	290	1,229
	23.6% water				
Combined vapors from evapora-	46.9% IPA				
tion of spent IPA wash	32.8% IBA	495	709	306	1,510
	20.3% water				
Water ^{1/}		---	---	19	19
Total		890	1,253	615	2,758
<u>Material out:</u>					
Distillate ^{2/}	80.5% IPA	81	1,181	205	^{4/} 1,467
	5.5% IBA				
	14.0% water				

TABLE 43.--Continued

Process stream	Analyses	IBA	IPA	HOH	Quantity
Bottoms ^{3/}	5.6% IPA	808	72	411	$\frac{4}{1,291}$
	62.6% IBA				
	31.8% water				
Total		889	1,253	616	2,758

^{1/} Combined feed presumably will be slightly deficient in the amount of water required to satisfy both azeotropes.

^{2/} Composition assumed to be 90 mole percent IPA azeotrope and 10 mole percent IBA azeotrope.

^{3/} Composition assumed to be 95 mole percent IPA azeotrope and 5 mole percent IBA azeotrope.

^{4/} Obtained by use of simultaneous equations.

TABLE 44.--Material balance over distillation column No. 3

(300 days per year, and 24 hours per day)

Basis: 1 hour

Process stream	Analyses	IBA	IPA	HOH	Quantity
		Pounds	Pounds	Pounds	Pounds
<u>Material in:</u>					
Spent anion regenerant ^{1/}	5.8% IBA	137	--	2,237	2,374
	94.2% water				
Water layer from desol-	1.8% IPA				
ventizer decanter	7.0% IBA	69	18	897	2,983
	91.2% water ^{2/}				
Total		206	18	3,134	3,357
<u>Material out:</u>					
Distillate	5.4% IPA ^{3/}	204	18	105	3,326
	62.5% IBA				
	32.1% water				

TABLE 44.--Continued

Process stream	Analyses	IBA	IPA	HOH	Quantity
		Pounds	Pounds	Pounds	Pounds
Bottoms-----	0.00508% IPA	2	<1	3,029	4/ 3,031
	.0592% IBA				
	Balance is water				
Total-----		206	18	3,134	3,357

1/ Only two-thirds of the total anion regenerant solution will be sent to distillation column No. 3. All alcohol removed by regenerant solution is assumed to appear in the first two-thirds portion. Composition was calculated on the basis $137/2,374 = 5.8$ percent IBA.

2/ Obtained from material balance over flash desolventizer.

3/ Composition and quantity of distillate was calculated assuming that both alcohols distill over simultaneously at compositions approaching those of their respective azeotropes with water.

4/ Calculated as difference between feed and distillate with total alcohol content set equal to 0.0156 mole percent.

TABLE 45.--Material balance over decanter for distillation columns
(300 days per year, and 24 hours per day)

Basis: 1 hour

Process stream	Analyses	IBA	IPA	HOH	Quantity
		<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>
<u>Material in:</u>					
Bottoms from distillation	5.6% IPA				
column No. 2	62.6% IBA	808	72	411	1,291
	31.8% water				
Distillate from distillation	62.5% IBA				
column No. 3	5.4% IPA	204	18	105	326
	32.1% water				
Total		1,012	90	516	1,617
<u>Material out:</u>					
Alcohol layer	74.7% IBA	993	82	254	1,329
	6.2% IPA				
	19.1% water				

TABLE 45.--Continued

Process stream	Analyses	IBA	IPA	HOH	Quantity
		<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>
Water layer ^{1/}	6.8% IBA	20	7	263	290
	2.4% IPA				
	90.8% water				
Total		1,013	89	517	1,619

^{1/} Composition and quantity obtained by use of ternary solubility diagram for IPA-IBA-H₂O system, Figure 15.



Fig. 1

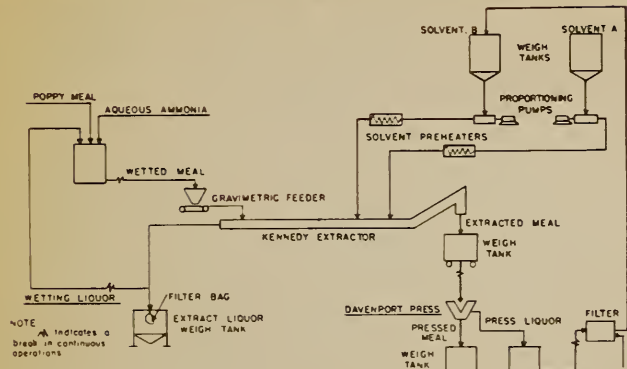


Fig. 3

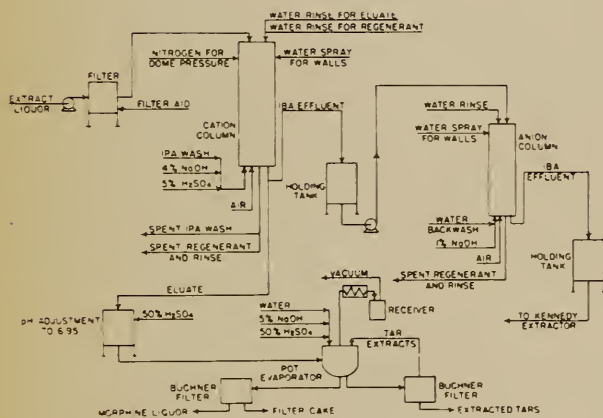


Fig. 5

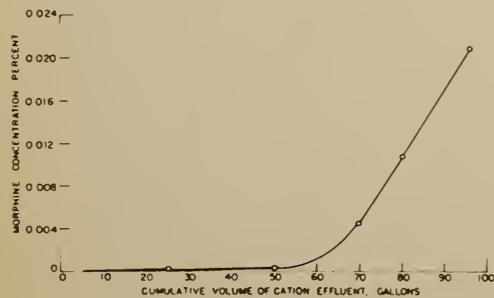


Fig. 7

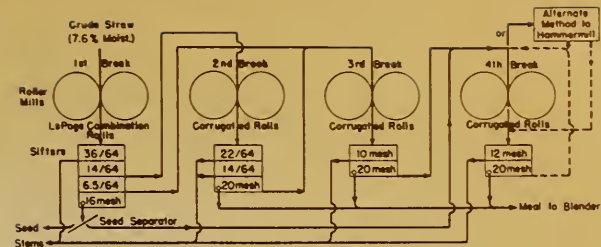
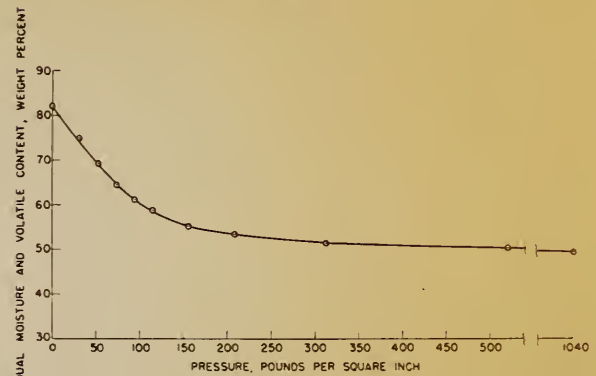


Fig. 2



EFFECT OF PRESSURE ON RESIDUAL MOISTURE AND VOLATILE CONTENT OF PRESSED MEAL.

Fig. 4

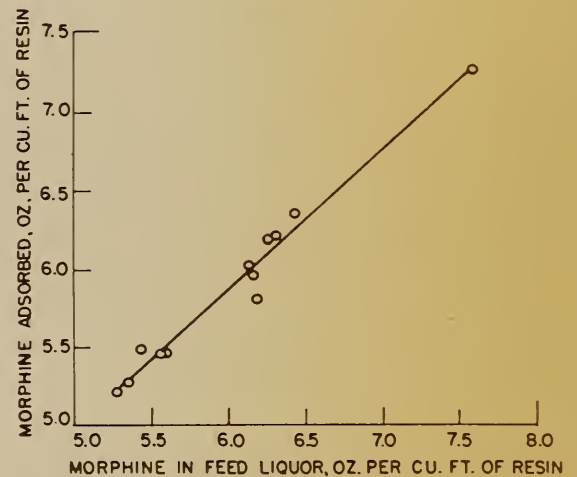


Fig. 6

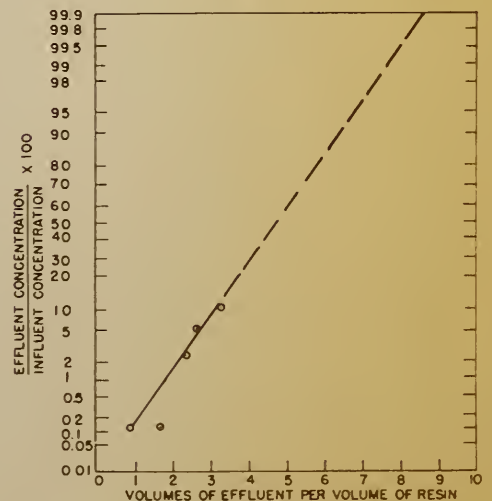


Fig. 8

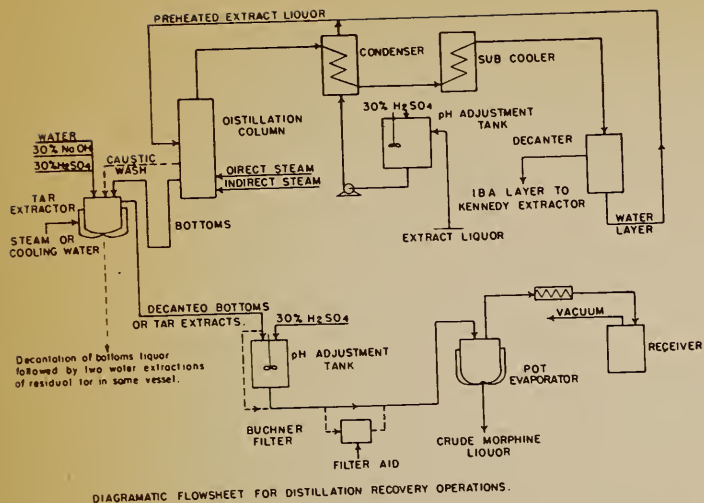


Fig. 9

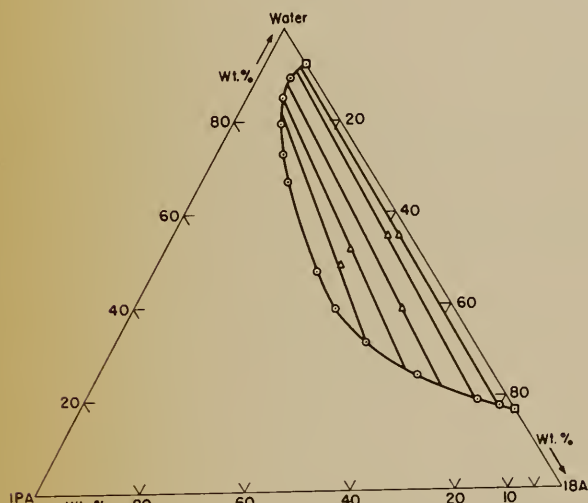
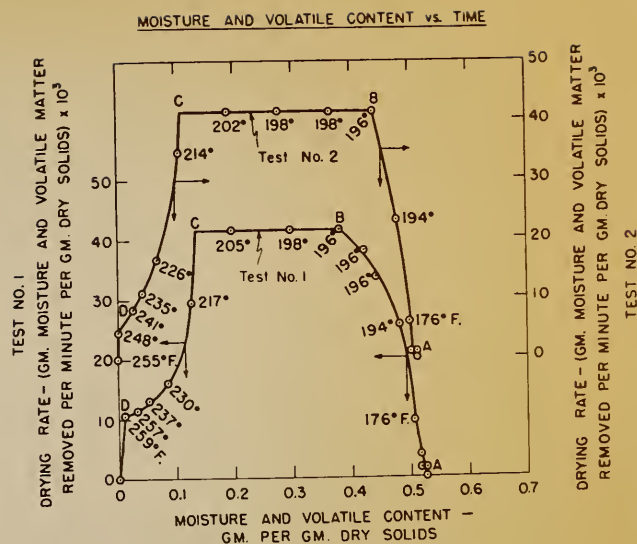


Fig. 11



DESOLVENTIZING RATE VS. MOISTURE AND VOLATILE CONTENT
Fig. 10

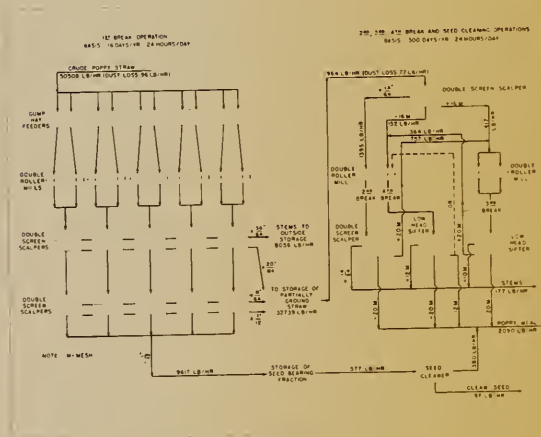


Fig. 12

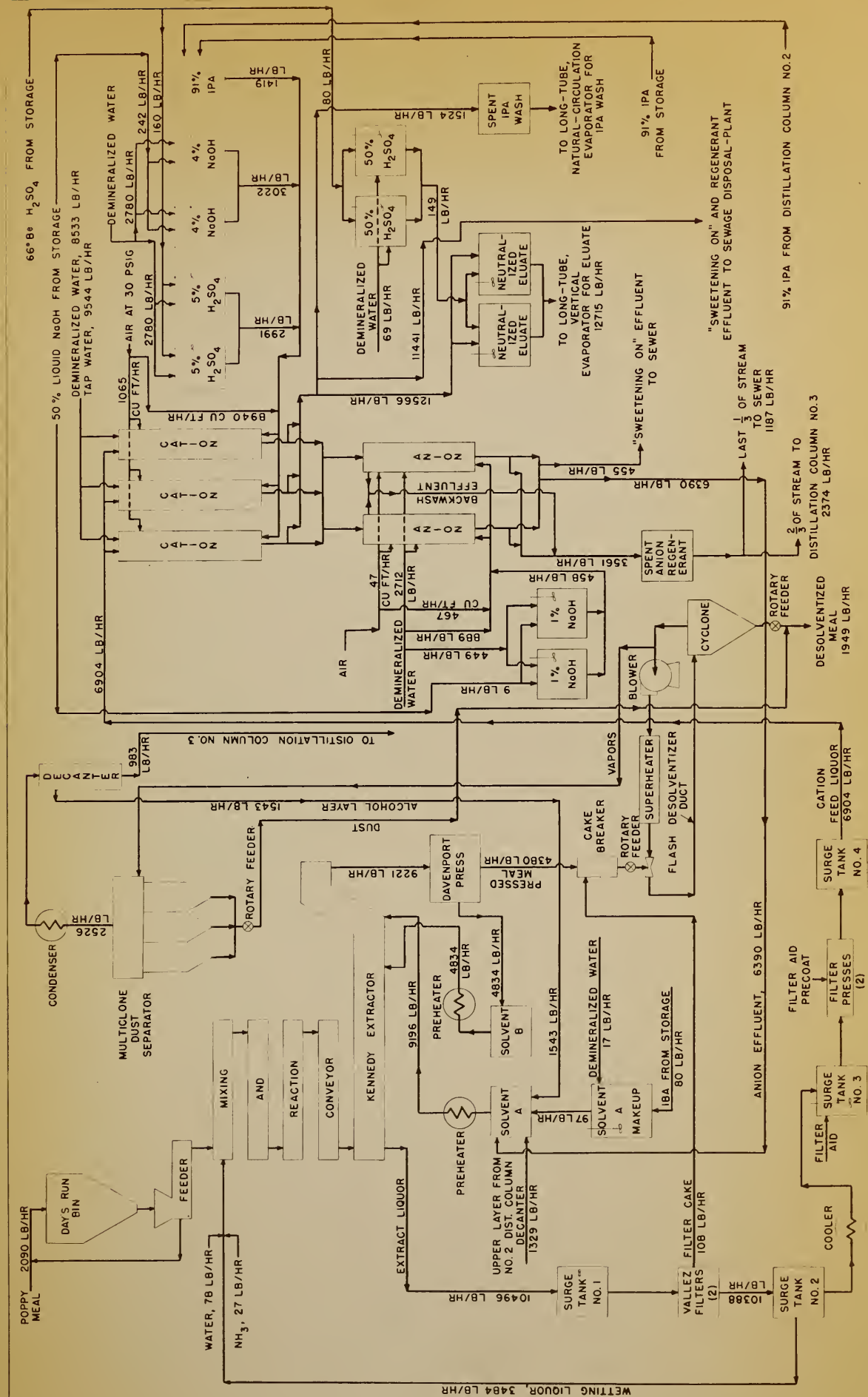


Fig. 13

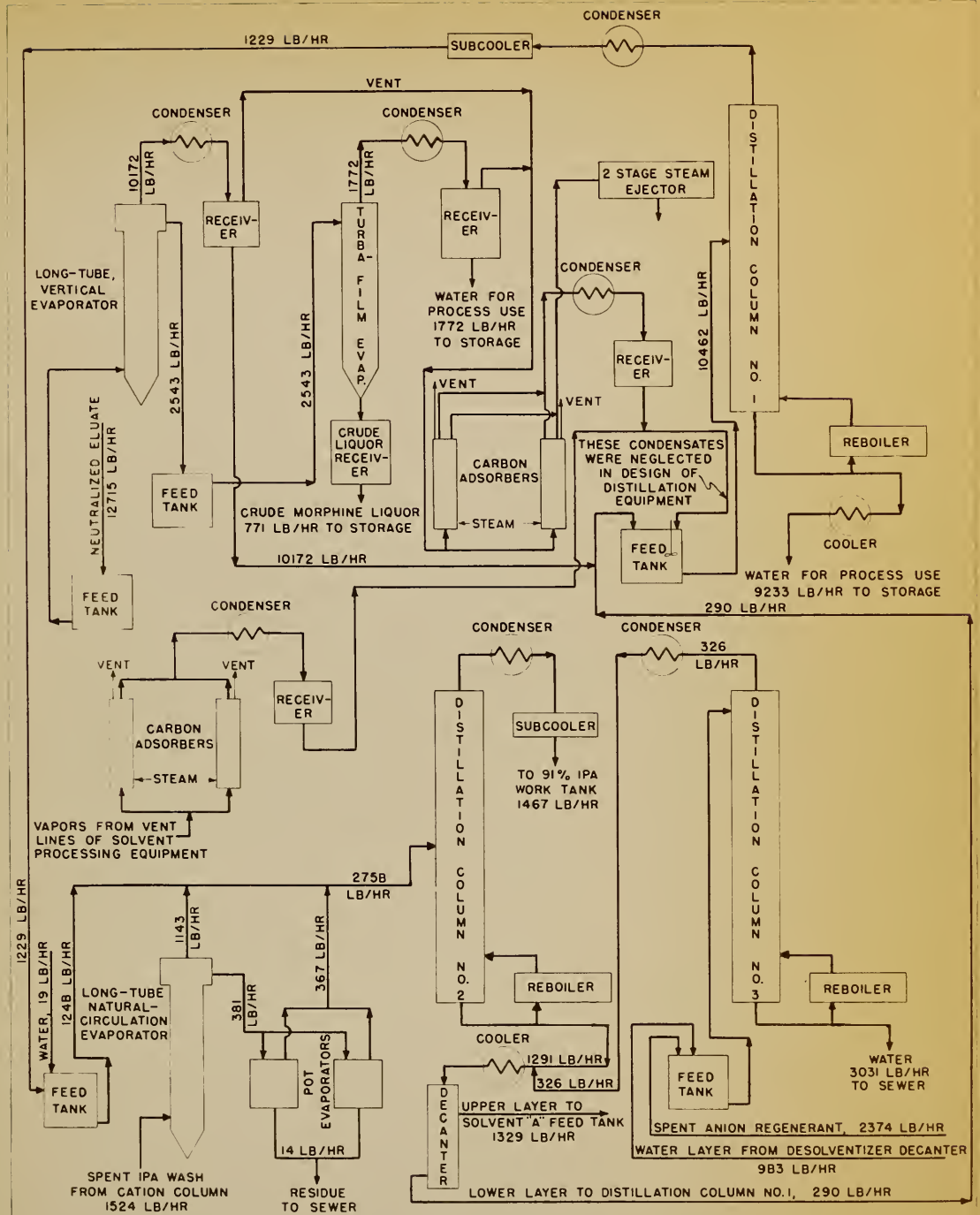


Fig. 14

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